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Thermal Stability of SrFeO₃/SiO₂/Si and SrFeO₃/Al₂O₃ Thin Film Systems:

Transmission Electron Microscopy Study of Interfacial Structures of the Thin Film Systems and Conductometric Sensing Response of SrFeO₃/Al₂O₃

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DEDICATION

This thesis is dedicated to my wife Fenglian Geng

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ABSTRACT

The literature review indicates that studies on the structures and properties of perovskites materials have shown attractive applications in the fields of energy, catalysts and sensing materials for fuel cell and sensing industries. Kinetic phenomena in thin film systems, such as solid state amorphization and interface reactions due to diffusion during thin film deposition, are introduced indicating that thermal stability is a concern in thin film sensor device application. The principle of traditional methods of materials characterization is briefly discussed. Emphasis is placed on the functions of analytical transmission electron microscopy.

The SrFeO₃/SiO₂/Si and SrFeO₃/Al₂O₃ thin film systems have been studied using transmission electron microscopy. The thin films of SrFeO₃ were grown by pulsed laser deposition. For the SrFeO₃/SiO₂/Si system, TEM characterization showed that the microstructure of the film deposited at room temperature contained crystalline and amorphous layers. Silicon diffusion into SrFeO₃ films occurred at the SiO₂ interface. The silicon-induced interfacial reactions resulted in phase transformations and the growth of complex crystalline and amorphous phases. The principal compositions of these phases were $Sr(Fe,Si)_{12}O_{19}$, SrO_x and amorphous [Sr-Fe-Si-O].

The films in the $SrFeO_3/Al_2O_3$ system were deposited onto single crystal and sintered polycrystalline Al_2O_3 substrates at room temperature and 700°C and subjected to annealing for various periods of time at 700-1000°C. TEM characterization showed that the morphology of the film varied with changes in deposition temperature: a columnar

structure was produced at room temperature and layers containing crystalline grains were produced at 700°C. The interfacial structures of the films remained unchanged below 700°C. Interfacial reactions were observed following annealing at 850°C for 5 hours. The phase transformation at the interface was characterized for the film annealed at 1000°C for 5 hours, for which the principal phases were identified as $SrAl_{2-x}Fe_xO_4$ and $SrFe_{12-x}Al_yO_{19}$. As a result, an isothermal section at 1000°C of a ternary phase diagram for SrO- Al_2O_3 -Fe₂O₃ is proposed. Evaluation for thin film conductometric sensing applications indicated that the untreated films deposited at 700°C onto both single crystal and sintered Al_2O_3 substrates exhibited a similar temperature dependency of conductivity in air and a *p*-type gas sensor response to oxygen and propane at 500°C.

ABRÉGÉ

Une recherche en littérature révèle que des études portant sur les propriétés des matériaux pérovskites ont démontrées la possibilité d'applications intéressantes dans les domaines de l'énergie, la catalyse, ainsi qu'entant que matériaux pour les pile à combustible et l'industrie des capteurs. Les phénomènes cinétiques dans les systèmes à couches minces, tel l'amorphisation en état solide, et les réactions aux interfaces dues à la diffusion pendant le dépôt de couche minces sont introduits, indiquant que la stabilité thermale est une considération importante dans le cas de l'application des couches minces dans le domaine des sondes. Les principes de la characterisation des matériaux par méthodes traditionnelles sont brièvement discutés, en mettant l'emphase sur les fonctions de la microscopie électronique en transmission (MET) analytique.

Les systèmes de couches minces $SrFeO_3/SiO_2/Si$ et $SrFeO_3/Al_2O_3$ ont été étudiées a l'aide de la MET. Les couches minces de $SrFeO_3$ ont été déposées en utilisant la méthode de dépôt par laser à impulsions. Dans le cas du système $SrFeO_3/SiO_2/Si$, la MET a démontrée que la microstructure de la couche mince déposée à la température ambiante contiennent des couches cristallines et des couches amorphes. Il y a eu diffusion du Si dans le $SrFeO_3$ à partir de l'interface du SiO_2 . Les réactions à l'interface induites par le Si ont menées à des changements de phase et à la croissance de complexes cristallines et de phases amorphes. Majoritairement, ces régions étaient composées de $Sr(Fe,Si)_{12}O_{19}$, SrO_x et de [Sr-Fe-Si-O] amorphe.

Les couches des SrFeO₃/Al₂O₃ ont été déposées sur des substrats mono-cristallins et du

Al₂O₃ poly-cristallin fritté, à la température ambiante et à 700°C, et ont été ensuite recuites à des températures entre 700°C et 1000°C pour des durées variables. La MET a révélées que la morphologie des couches dépend de la température de déposition, soit une structure de colonnes dans le cas des dépositions à la température ambiante, ou des couches contenant des grains cristallins en rangé dans le cas des dépositions à 700°C. Des réactions aux interfaces suite à un recuit à 850°C d'une durée de 5 heures ont été observées. Les changements de phase à l'interface ont été characterisees dans le cas de la couche recuite à 1000°C pour 5 heures, et les phases dominantes identifies sont le SrAl₂. _xFe_xO₄ et le SrFe_{12-y}Al_yO₁₉. Suite a ces observations, une partie isotherme à 1000°C du diagramme de phase du SrO-Al₂O₃-Fe₂O₃ est proposée. Suite à une évaluation des couches déposées à 700°C, sur les deux types de substrats, n'ayant pas été recuites, à fin d'application possible en sonde conductométrique, il a été observe que la conductivité en air ambiant des couches avaient une dépendance thermal semblable, et que les couches avaient une réponse de type-p à l'oxygène et au propane à 500°C.

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Chapter 1

Introduction

1.1. Background information

Perovskite (CaTiO₃), discovered in the Ural mountains of Russia by Gustav Rose in 1839 and named for russian mineralogist, L. A. Perovski (1792-1856), has become the name of a more general group of crystals ABO₃, where A and B are cations of different sizes. Perovskite and its related oxides represent one of the numerous families of transition metal oxides. Early studies have shown that the interrelationships of the structural and thermodynamic properties of the phases in the bulk powder state are a function of temperature and oxygen partial pressure.^[1] Phase transformation among them is identified using differential thermal analysis (DTA), thermogravimetric analysis (TGA) and Mössbauer spectroscopy, ^[2, 3] indicating that perovskite is non- stoichiometric in oxygen. The study of the bulk electrical conductivity of the SrFeO_{2.5+x} (0<x<0.5) system showed that the material is a *p*-type semiconductor within a certain range of temperature and partial oxygen pressure $\{P_{(O2)}\}$ with the conductivity of SrFeO_{2.5+x} increasing with increasing $P_{(02)}^{[4]}$ suggesting that this physical property can be used as a transduction signal for sensor applications. As a result, perovskite and its related oxides have attracted considerable interest. Efforts from researchers have been made on its extensive applications in a number of technological areas such as materials for catalysis^[5] and solid state gas sensors.^[5-10]

SrFeO_{2.5+x} materials can be used as thin film gas sensors [1, 8, 9, 11], since the reversible

uptake of oxygen at elevated temperatures can readily occur and is accompanied by significant changes in electrical conductivity which can be monitored as the sensor transduction signal. However, the electrical and gas sensing properties of films of these material types are strongly dependent on the cation and oxygen stoichiometries^[9] and film morphology.^[12-15] For example, films with amorphous or texture crystal structure cannot easily reversibly transform from the brownmillerite (at $x \sim 0$) to the cubic perovskite structures (at x > 0.4), therefore, they show limited sensor functionality.^[16, 17]

SrFeO₃ thin film gas sensors have high sensitivity and rapid response to the changes of gas pressure at around 350°C-500°C. However, the SrFeO₃ thin film as a part of a sensor system together with its substrates has to undertake such a high operation temperature and must be durable at this temperature in order to maintain its consistency of functionality. Therefore, thermal stability of the thin film system of the sensor with substrate is critical. This is because the perovskite materials may be unstable under certain thermo-chemical conditions,^[18] or at elevated operating temperatures. In the ceramic-based gas sensors, interfacial reactions may occur, which means the films may react with the underlying substrate. ^[19-25] Variations in microstructure and chemical composition of the thin films could result in failure of signal production, suggesting that thermal stability of the thin film system must be taken into account in determining sensor stability and design in order to ensure longer term signal reproducibility. Thus, it is essential to have a full understanding of the effects of deposition conditions, especially the deposition temperatures and post-deposition thermal treatments on the changes of interfacial structures of thin film systems.

1.2. Research objectives

The crystal structure and phase transformation of perovskite thin film materials mentioned above are mostly studied by x-ray or thermal analysis; neither can provide a direct view of the crystal structure and explore the nature of the relationship of structure vs. properties. Therefore, one of the purposes of this study is to use TEM techniques to reveal the characteristics of the perovskite thin film materials and their interaction with substrates.

In addition to the sensitivity and rapid response, thermal stability of the thin film also has to be taken into account. This is because a gas sensor has to be durable in an environment with relatively elevated temperature. The crystal structure should have no change due to diffusion during the thermal traetment. Therefore, knowing the thin film sensor material and interfacial reactions between the thin films and substrate becomes the first priority of the study. In the present work, interfacial reactions between the SrFeO_{2.5+x} thin films grown by pulsed laser deposition (PLD) techniques onto single crystalline silicon, single crystal alumina (sapphire) and polycrystalline alumina (sintered alumina) substrates, and subjected to thermal treatments, were investigated using transmission electron microscopy (TEM).

1.3. Brief description of the thesis

The thesis is divided into 8 chapters. Following this Introduction section (Chapter 1), Chapter 2 is a brief overview of perovskite materials including their crystal structures, properties, applications, material characterizations and thin film sensor structures. A brief discussion is made of kinetic phenomena in thin films such as amorphization and interfacial reactions. In chapter 3, experimental methodology applied in the thesis study is described theoretically and practically. The main body of the thesis is constructed with three chapters, i.e., chapters 4-6. Presented in chapter 4 is the study of the thermal stability of the SrFeO₃/SiO₂/Si thin film system using TEM. Chapter 5 is focused on the TEM investigation on the thermal stability of SrFeO₃ /Al₂O₃ thin film systems, and the evaluation of the gas-sensing response for conductometric sensing applications for SrFeO₃/Al₂O₃ thin film system is reported and discussed in this chapter. Conclusions for the investigations on the SrFeO₃/SiO₂/Si and SrFeO₃ /Al₂O₃ thin film systems are summarized in Chapter 6. Original contributions to knowledge are described in Chapter 7. Following chapter 7 are the recommendations for future studies as the last chapter, Chapter 8.

Chapter 2

Literature Review

In order to build a bridge between microstructure and the properties of perovskite materials, it is necessary to learn the basic knowledge about perovskite and to reveal the research front about perovskite materials. This will include the fields of crystal chemistry, physical properties, applications of perovskite materials and the techniques used to discover the internal world of these materials. Crystal chemistry of perovskite materials is fundamental since it studies not only the crystal structure of the materials, but also the nature of bonding in them.

In the first part of this review, the structures and structure defects of the perovskite and its related materials as well as crystal characterizations of perovskite material are overviewed. In the second part, the electronic properties are discussed. Given in the third part of the review is the brief introduction of the basic applications of perovskites-type oxides as solid state chemical sensors. In the last part of the review, thin film system related theories are discussed.

2.1. Structure of perovskites family of oxides

2.1.1. Stoichiometric perovskites, ABO₃

The mineral $CaTiO_3$ is named perovskite, accordingly all oxides having the general formula ABO₃ and structures similar to that of the mineral are called perovskite related. The stoichiometric perovskites (ABO₃) has a cubic or pseudo-cubic structure with the B atoms (titanium atom in CaTiO₃) taking the corner position and A atoms (calcium in CaTiO₃) in the cubic center (Figure 2.1.1a). If a perovskite ABO₃ is close-packed structure, it can be considered as having a host lattice of $[BO_3]_{\infty}$ with corner-sharing BO₆ octahedra, and forming cages bonded by 12 oxygen atoms where *A* cation is present. The superposition of the cages along the <100> direction makes it possible to describe these oxides by a tunnel structure with a square cross-section shown in Fig. 2. 1.1b, where the solid dots represent cation A, the points of intersection of three lines are the positions of oxygen atoms; the points of intersection of two lines are the positions for cation B. The largest tunnel is in between A and B shown in Fig. 2.1.1b. Stoichiometric perovskites have been systematically studied by Gallasso,^[26] and its tabulations are available in the literature.^[27,28]



Fig. 2.1.1. (a) ABO₃-type structure: B is at the corners of the cubic cell; A at the center. (b) Projection of the structures along <001> showing the existence of tunnels with a square section.

According to the valence of the A and B elements, stoichiometric ABO₃ perovskites can be classified into three categories:

a. $A^{I}B^{V}O_{3}$ (A = Na, Ag, K, and more rarely Rb, Tl, Cs; B = Nb, Ta, I),

b.
$$A^{II}B^{IV}O_3$$
 (A = Ba, Sr, Ca, Pb, and more rarely Cd; B = Ti, Zn, Zr, Hf, Mn, Mo,
Th, Fe, Ce, Pr, U), and

c.
$$A^{III}B^{III}O_3$$
 (A = Ln, Bi, Y; B = Fe, Cr, Co, Mn, Ti, V, Al, Sc, Ga, In, Rh).

Many of the ferroelectric perovskite oxides belong to the first two series and are characterized by a small distortion of the cubic cell. A typical example is that of barium titanate, BaTiO₃. A shifting of the titanium from the center of the "O₆" octahedron results in a tetragonal cell at room temperature, and leading to a noncoincidence of the gravity centers of positive charge (cations) and negative charges (anions) (Fig. 2.1.1c),^[29] giving rise to dipoles, which can be reversed in an electric field, hence to ferroelectricity.



Fig. 2.1.1c. Tetragonal BaTiO₃ showing distortion of the TiO₆ octahedron.^[29]

Most of the compounds in the third series are the GdFeO3-type perovskites, which exhibit

the same kind of distortion. They are orthorhombic (Fig. 2.1.1d) with lattice parameters:

 $a \approx a_p 2^{1/2}$, $b \approx n a_p 2^{1/2}$, $c \approx 2 a_p$

where n is integer, a_p represents the parameter of the cubic cell of the perovskite.



Figure 2.1.1d. The orthorhombic structure of GdFeO₃. The Fe^{3+} ions are in octahedral coordination.^[26]

Complex stoichiometric perovskites are formed if two or more metallic elements are located in the octahedral B sites. When the B sites are occupied by two elements simultaneously, ordering between the two ions can be observed leading to multiple perovskite cells. This family can be classified in three categories:

a.
$$A^{III} \left(B^{III}_{0.67} B^{VI}_{0.33} \right) O_3$$
 (A = Ba, Sr, Pb; B^{III} = Ln, Sc, Fe, Cr, In; B^{VI} = W,U, Re),

b.
$$A^{II} \left(B^{II}_{0.33} B^{V}_{.0.67} \right) O_3$$
 (A = Ba, Sr, Ca, Pb; B^{II} = Ca, Cd, Co, Ni, Cu, Fe, Mn, Zn;

$$B^{V} = Nb, Ta$$
) and

c. $A(B_{0.5}^{'}B_{0.5}^{"})O_3$, where A, B' and B' possess various oxidation states including: $A(B_{0.5}^{III}B_{0.5}^{V})O_3$ (A =Ba, Sr, Ca, Pb; B^{III} = Ln, Y, Bi, Fe, Mn, Se, Rh, Ni, Al, Ga, In; and B^V = Nb, Ta, Pa, Sb, Re, W, Os),

$$A^{II} (B^{II}_{0.5} B^{VI}_{.0.5}) O_3$$
 (A =Ba, Ln, Sr, Pb; B^{II} = Cu, Co Re, Mg, Mn, Ni, Zn, Cd, Ca;
B^{VI}= W, U Mo, Re, Os),
 $A^{II} (B^{I}_{0.5} B^{VII}_{.0.5}) O_3$ (A = Ba, Ca, Sr; B^I = Li, Na, Ag; B^{VII} = I, Os, Re), and
 $A^{III} (B^{II}_{0.5} B^{IV}_{.0.5}) O_3$ (A = La, Nd; B^{II} = Mg, Cu, Ni, Co, Zn; B^{IV}= Ir, Nb, Ti, Ru).

The Compounds in the first category, which have twice the number of B(III) ions than B(VI) ions, are generally characterized by a cubic cell, with an a parameter double that of the perovskite ($a \approx 2 a_p$). The B site ions are ordered in such a way that two different B ions are alternately at the corners of the perovskite subcell. Most compounds in the series of $A^{II}(B_{0.33}^{II}B_{0.67}^{V})O_3$ possess a different kind of ordering of the B site ions, leading to a hexagonal cell ($a \approx a_p 2^{1/2}$, $c \approx a_p 2^{1/3}$). Its structure can be described as a close packed stacking of AO₃ layers parallel to the <111>_c (c stands for cubic) plane of the ideal cubic perovskite, the B ions being distributed in an ordered way in the octahedral cavities between these layers. The size difference between the B^{II} (e.g., Sr) and B^V ions (e.g., Ta) is the explanation of the ordering, where two B(V) planes alternate with one B(II) plane along <111>c. The last group $A(B_{0.5}^{III}B_{0.5}^{V})O_3$ perovskites are characterized by various ordering of the cations on the B site.

The factors affecting the stability of the perovskite structure are:

- a. the relative sizes of the A and B elements.
- b. the electronic configuration of the *B* sites ions.

In the perovskite structure, the relative sizes of the A and B elements affect the stability of

the perovskite structure. The ionic radius of the *A* cation normally is larger than that of the *B* ion. On the basis of geometric considerations, Goldschmidt ^[30] introduced a tolerance factor, *t*, to define the size limits of the ions. The tolerance factor *t* is obtained by considering the structure as derived from a close-packed stacking of the *A* and oxide ions. It is generally defined by the relationship $R_A + R_0 = t 2^{\frac{1}{2}} (R_B + R_0)$, where R_A, R_B and R_0 are the radii of the respective ions A, B and oxygen. The ideal close packing is at t = 1. For the perovskite structure, *t* ranges from 0.8 to about 1.1. For t > 1, the space available in its "O₆" octahedron is large enough for B ion. At t < 0.8, it corresponds to a similar size of A to B ions, leading to more close-packed structures. The tolerance factor is approximate and empirical, although it is useful to predict the occurrence of the perovskites structure, the electronic structure of the B ions in the perovskite structure is not obvious.

2.1.2. Nonstoichiometric Perovskites A_xBO₃

In nonstiochiometric perovskites, A_xBO_3 , cationic defects in the cages (A site) can vary from zero (ReO₃-type structure) to unity (stoichiometric perovskites) depending on the nature of the A and B ions. For instance, Na_xWO₃ is the prototype of the most important family of the tungsten oxide bronzes, A_xWO_3 , which have been synthesized for A = Li, Na, Ca, Sr, U, Cd, Hf. The name bronze was given to such oxides because their physical properties were similar to those of alloys. The oxides exhibit a wide homogeneity range like alloys (solid solutions) and varied metallic conductivity or semiconducting behavior. By the incorporation of the A cations, the electrons are introduced in the host lattice, [WO3]_∞ and delocalized in the octahedral framework, giving rise to the mixed valency of tungsten W(VI)-W(V). The composition range is wide ($0 \le x \le 1$) for univalent cations but narrowly for trivalent and tetravalent cations, (x < 0.1). Table 2.1.2 shows that the extent of incorporation, x, in A_xWO₃ bronzes is not related directly to the size of the A ions.^[31] The range is narrow for bivalent cations (x < 0.05). The nature of the crystallographic cell depends on the nature of the A cation and also on the value of x. Lithium and lanthanide bronzes are cubic, whereas the sodium ones are cubic for high x values and tetragonal for low x. Different types of distortion of the perovskite cell are observed for divalent and tetravelent A cations.

Bronze	Composition	Symmetry	Unit cell dimensions
Li _x WO ₃	0.31< x < 0.57	Cubic	a is variable (≈0.37nm)
Na _x WO ₃	0.26< x < 0.93	Cubic	a is variable (~0.38nm)
Na _x WO ₃	x = 0.10	Tetragonal	a = 5.25, c = 0.390nm
Cu _x WO ₃	0.26 < x < 0.77	Orthorhombic	a = 0.388, b = 0.373, c = 0.774 nm
		at $x = 0.26$,	
		Triclinic	a = 0.585, b = 0.665, c = 0.488 nm
		at $x = 0.77$	$\alpha = 135.7^{\circ}, \beta = 91.7^{\circ}, \gamma = 93.6^{\circ}$
La _x WO ₃	0.67 < x < 1.0	Cubic	a is variable (≈0.39nm)
Sr _x WO ₃	0.7 < x < 0.95	Cubic	a is variable (≈0.40nm)

Table 2.1.2. Cubic and Pseudocubic Perovskite Bronzes $A_x BO_3^{[31]}$

Besides the bronzes, nonstoichiometric perovskites A_xBO_3 with insulating properties are known and called bronzoids because of their wide homogeneity range and similarity of structure. These dielectric materials are isotopic with the bronzes. The symmetry of the perovskite cell depends on the value of x. One have observed several types of distortion of the structure for WO₃ (a type of A_xBO_3 at x=0). Distortion of the octahedra results in the different symmetries of the perovskite cells because B site tends to adopt a 4+2 coordination resulting in distortion and the tilting of the octahedral. Therefore, the perovskite cages become flattened.

2.1.3. Oxygen-deficient perovskites

The formation of ordered anionic vacancies in the host lattice of perovskites leads to new mixed frameworks in which the BO₆ octahedra share their corners with polyhedra involving a smaller number of apices: pyramids, tetrahedral and square-planar units. Several series of ternary oxides, involving copper, manganese, cobalt, and iron, illustrate these structural types derived from the distinctive feature of perovskite.^[32, 33]. The formation of anionic vacancies in the perovskites $ABO_{3.x}$ is dependent on the ability of the *B* cations to adopt several coordinations (besides the octahedral one) and they also must exhibit mixed valence, e.g., Fe(III)/Fe(IV), Cu(II)/Cu(III), Mn(III)/Mn(IV). (ABO₃)_nABO₂ represents the Brownmillerite Family. The systems Ca₂Fe₂O₅-ATiO₃ (A = Ba, Sr, Ca) and Ca₂Fe₂O₅-AfeO₃ (A = Y, La, Gd) are characterized as the ABO_{3-x} oxygen-deficient perovskites. These phases are represented by the general formula (ABO₃)_n, resulting from the creation of ordered anionic vacancies in the octahedral framework [BO₃]_∞ · ABO₂.

2.1.4. Characterizations of perovskites materials

There are many techniques for materials crystallographic characterization. In this section the discussion will be focussed on the most commonly used physical techniques: (a) diffraction including x-ray diffraction and electron diffraction, and (b) high resolution imaging by transmission electron microscopy.

a. Diffraction: x-ray and electron diffraction are widely used in the characterization of perovskite materials. Powder x-ray diffraction has been used in almost all the characterization of perovskites, such as determination of crystal structure, structure

defects and phase transformation.^[34-35] Electron diffraction (ED) is used in the investigation of the crystal structure of perovskites materials. The unique advantage of electron diffraction is that electrons interact strongly with matter and diffraction patterns are obtained from a very small area, providing information about local crystal structure. Particularly, electron diffraction is powerful on determining the crystal structure of unknown materials through interpreting the symmetric information of crystal structure from their diffraction patterns. Long-range ordering and complexity of structure characterized with ED frequently occur in the electron diffraction of perovskite type of materials, such as characterising the existence of twins, the inhomogeneity of the arrangement of the structural features, where satellite diffraction occurs and distinguishable types of ED pattern from different areas of the same crystal can be observed (Fig 2.1.4a).^[36]

b. Electron microscopy (EM): EM has been used in the characterization of perovskites for many purposes including the study of crystal structure and order-disorder phenomena of perovskite materials. For instance, scanning electron microscopy (SEM) is widely used for providing morphological images of samples over a wide range of magnification, for studying the texture (by electron backscatter diffraction), topography and surface features of powders or fragments in definitive 3D quality images because of the depth of focus possible with SEM instrumentation. High-resolution transmission electron microscopy (HRTEM) is capable of giving information on an atomic scale. Crystal defects such as dislocations, stacking faults, antiphase boundaries and twin boundaries may be seen directly using TEM imaging. The domain structure of ferromagnetic and ferroelectric materials may be observed. With HRTEM, variations in local structure such as site



Fig. 2.1.4a. An ED pattern with satellites arising from misorientation of two superposed lamellae of $BiPbSr_2YCu_3O_8$ crystal.^[36]

occupancies and vacancies can be observed directly. HRTEM can provide explicit images in identification of order–disorder phenomena in pervoskite materials ^[37-40]. Fig. 2.1.4b is a HRTEM micrograph of a superconductor YBa₂Cu₃O_{6.66}.^[39] In the middle of the micrograph, a disordered area without any preferential direction can be observed. The variations in the spacing of the rows of white spots and defects appear as the termination of rows of atoms. The structure rearranged during observation with the microscope (as a result of heating) suggesting that metastable areas existed, where the local ordering of oxygen is not achieved. The projected structures in the regular and ordered areas of the crystal are directly interpretable.

Another example of HREM study is in intergrowth mechanisms. In the studies of intergrowth of tungsten bronzes ^[41-43], phosphate tungsten bronzes or hexagonal perovskites ^[44-46], HREM played an essential role in the recognition of complex structures. Such an investigation needs a profound knowledge of the basic structures as



Fig. 2.1.4b. a [001] HRTEM image of $YBa_2Cu_3O_{6.66}$ showing variations in the spacing of the rows and their undulation.^[39]

well as of the corresponding HREM images, as an example shown in Fig. 2.1.4c. The general formula $(AO)_n(A'CuO_{3-x})_m$ is used to express the molecular building principles of the superconducting cuprates. Its ionic distribution appears to be directly correlated to the nature of the cation associated with the alkaline earth ions. The structure is characterized by both triple and double rock-salt (RS) layers.

Shown in fig. 2.2.4c are idealized $(AO)_n(A'CuO_{3-x})_m$ structures built up from a double perovskite layer (m = 2) and intergrown with one, two, three or more rock-salt-type layers, corresponding to n = 1, 2, 3, ..., n, respectively. Fig.2.2.4c is a schematic drawing where A and A' represent cations without taking into account their nature. When n is an even number the median AO layer (arrowed layer in Fig 2.1.4c (b) plays the part of a mirror and thus the c parameter can easily be calculated. The parameters of the different members of the various families can be expressed as:



Fig. 2.1.4c Idealized drawing of $(AO)_n(A'CuO_{3-x})_m$ structures. (a, c) rock-salt-type layers built up from AO layers (n = 1, 3, m=2). (b) corresponding intergrowth phases built up from double oxygen deficient perovskite layers (m = 2) and rock-salt-type layers (n = 2).^[44]

 $a \sim b \sim a_p$, $c = na_r + ma_p$, (for materials with P type space group)

On the other hand, when n is an odd number, the mirror disappears and one observes a shifting, (a + b) / 2, of alternate complete slices (rock-salt and perovskite-type layers). the c parameter is doubled and the atomic positions imply an I-type space group

 $a \sim b \sim a_p$, $c = (na_r + ma_p) \times 2$, (for materials with I type space group)

where a_p is the thickness of a perovskite layer and a_r is the thickness of a rock-salt type layer. Note, P and I stand for primitive and body centered Bravais lattice respectively.

The indication of the n value in HRTEM images is determined by a shifting of one slice with respect to the adjacent ones. The m value is more difficult to determine in these structures due to the oxygen-deficient character of the perovskite layer and the possible substitutions of the calcium ions by either thallium or strontium. Two types of images are important and have to be recorded during the observations. Shown in Fig. 2.1.4d is



Fig. 2.1.4d. Significant images usually used during contrast interpretation. Left: close to the Scherzer value. Right: defocus value close to -700Å, where the white dots are correlated to the heavy atom positions.^[44]

the [100] HRTEM images of compound $[Tl(Bi)O]_n$ - $[BaCuO_3]_m$. Some of them are collected together shown in Fig. 2.1.4d for easy comparison. These images are taken from the through-focus series close to the Scherzer value so as to show reverse contrast in both the bismuth and thallium families. In the first column, for defocus close to – 400nm, the bismuth or thallium atoms appear as dark dots while the white dots correspond to the oxygen or vacancy positions. In second column, for defocus close to –700nm, the cations
are highlighted and heavier cations Bi or Tl and Ba appear brightest.

It should be noted that simultaneous occupation of the cation site in the rock-salt layer by two different atoms (Pb/Ca, Pb/Sr, Sr/Nd, etc.) results in a more complex contrast; the interpretation of the image contrast must then be considered for each family. It also possible that the [001] projection of these structures shows no information about the nature of the layer stacking owing to the superposition of both cation and anion positions.

2.2. Electronic properties of perovskites

2.2.1. Electronic properties of transition metal oxides

Transition metal oxides can be divided into two classes by distinguishing their electron configuration. The oxides in the first class are those in which the metal ion has a d^o electronic configuration. In these oxides, the oxygen 2p valence band is filled and the metal d conduction band is left empty (the energy gap of around 3-5eV). High purity oxides of this class exhibit intrinsic electronic conduction only at high temperatures. With the d^o cations at octahedral site, the oxides exhibit spontaneous ferroelectric distortions (e.g., WO₃). At high temperatures, many of them become nonstoichiometric due to loss of oxygen. Oxygen loss or insertion of electropositive metal atoms into these oxides promotes electrons to the conduction band. The nature of electronic conduction in these materials depends on the strength of electron-phonon coupling and the width of the conduction band derived from metal *d* states. When the coupling is large and the band is narrow, small polarons are formed and such materials (e.g., Na_xV₂O₅) exhibit hopping (tunneling) conduction. When the conduction band is broad, the material (e.g., Ba_xWO₃)

exhibits metallic properties. The other classes of the transition metal oxides are those in which the d shell is partially filled. These oxides can be metallic or insulating. Some of them exhibit temperature-induced nonmetal-to-metal transitions. Perovskite structures belong to the isostructural series of transition metal oxides, exhibiting systematic changes in electronic properties^[47-52]

2.2.2. Electronic properties of perovskites

The perovskite structure is distinguished by 180° cation-anion-cation <u>interaction</u> of octahedral site cations (Fig.2.2.2a). Less possibility of cation-cation interaction is obvious because of the large separation along the face diagonal. The variety in the properties of perovskites is illustrated by the following examples:

BaTiO₃ is ferroelectric.

SrRuO₃ is ferromagnetic and conductive

LaFeO₃ is weakly ferromagnetic.

 $BaPb_{1-x} Bi_x O_3$ is superconducting,

LaCoO₃ shows a nonmetal-to-metal transition.

ReO₃, A_xWO₃, LaTiO₃, AMoO₃ (A = Ca, Sr, Ba), SrVO₃ and LaNiO₃ perovskite oxides exhibit metallic conductivity; which is due to the strong cation-anion-cation interaction. A perovskite structural matrix has been tabulated by Goodenough, et al. (Fig. 2.2.2b).^[48] The important perovskite oxides containing transition metal ions at the B-site are listed. The oxides with the same *d* electron configuration are grouped together in the columns. The entries in each column are arranged in decreasing order of B cation-anion transfer energy *b* (B-O covalency) from top to bottom. Covalent mixing parameters λ_{σ} and λ_{π}



Fig. 2.2.2a. The possibility of cation-anion-cation interaction along the cube edge of perovskite structure.^[26]

(and therefore the transfer energies b_{σ} and b_{π}) increase with the increasing oxidation state of the B cation.

2.3. Applications of perovskite-type oxides ABO₃

2.3.1. Applications of perovskite-type oxides ABO₃ as solid state chemical sensors

Chemical sensors have the potential to play a crucial role in meeting environmental objectives through applications in several respects, this role would make use of a number of the advantages of chemical sensors, such as their relatively low cost, and capability for miniaturization. Examples of applications include enlarging existing monitoring and measurement networks to expand monitoring coverage and to survey areas that may require more detailed monitoring. The application could also include optimizing energy and material used in process control, thereby minimizing emissions.



Fig. 2.2.2b. Oxide perovskites with transition metal ions in different electron configurations.^[48]

a. Measurement of response an sensitivity of sensors

Chemical sensors based on conductometric transduction must provide sufficient sensitivity in order to realize this potential. The basic measurements for sensing functionality are the response and sensitivity properties which are defined as follows:

(a) The resistance ratio: R_{air}/R_{gas} ,

where R_{air} and R_{gas} are the resistances in air and in an atmosphere containing a constant gas concentration, respectively;

(b) The response ratio: $(R_{air}-R_{gas})/R_{air} \ge 100\%$,

where R_{air} and R_{gas} are the resistance in air and after exposure to a flammable gas,

respectively.

(c) The sensitivity of the sensor is defined as the slope of the output characteristic curve of response with a change in concentration, i.e.:

Sensitivity
$$\approx \frac{\partial (R_g / R_a)}{\partial [conc.]_g}$$
, where [conc.]_g is gas concentration.

More discussion about sensitivity is highlighted in chapter 5.

b. Structure of gas sensor

A number of perovskite-type oxides (ABO₃) were used as gas sensor materials because of their thermal and chemical stability. Fig.2.3.1a schematically shows the simple structure of gas sensors. The layer of semiconductor oxide used as a gas sensor is covered with ceramic insulation tube assembled with a heater, lead wires, lead pins, insulating substrates and stainless steel net. The gas sensor is placed in the center of the apparatus cell (a flow-type or a closed-type) containing controlled fresh air, which can have analyzed gases introduced.

c. Gas Sensor in a sensing system

The principle of a gas sensor is based on changes in electrical resistance which are caused by adsorption of a gas on the surface or bulk of semiconductor oxides. Fig. 2.3.1b schematically shows the principles of chemical sensing. If a gas (i.e., alcohol, carbon monoxide, hydrogen or hydrocarbon etc) is injected into the sensor (5), after handling and catalyzing (refer 1, 2, 3, 4 in Fig. 2.3.1b), the resistance of the semiconductor will change. The signal output then is treated by a complex electronic system. In order to obtain electrical characteristics of the sensors, a fixed d.c. current is applied to the sensor and the change of sensor resistance is monitored by measuring voltage changes. In general the sensitivity of the sensor is influenced by the operating temperature and the



Fig. 2.3.1a. Schematic diagram of typical sensor structure.

concentration of gases and materials used. When a reducing gas, for example, is introduced into the system, a conductivity change in the thin oxide film is observed. A specific example of conductivity change in flow system is shown in Fig. 2.3.1c. For the SmCoO₃ thin film, the conductivity decreases immediately after the injection of methanol and then is restored to its initial value. Since the conductivity changes under adsorption of reducing gas occur on the surface of gas sensors, it is necessary to consider the catalytic reaction on the surface of perovskite oxides. Catalysis activity is essential for nearly all metal oxide based gas sensor materials. T. Arakawa ^[54] showed a link between energy gap ΔE and the activity of the sensing materials, i.e. $\Delta E = E_c - E_t$, where E_c is the energy of the conduction band, and E_t is the energy of the surface state. ΔE is called apparent activation energy, The apparent activation energy (ΔE) can be estimated from the conductivity changes after the injection of methanol, by using equation $\sigma = A \sigma_0 \exp (-\Delta E / kT)$, where σ is the minimum conductivity after the adsorption of a reducing gas,



Fig. 2.3.1b. Schematic illustration of a sensing system.

 σ_0 is the conductivity in a steady gas flow, A is a constant.^[55] The results are summarized in table 2.3.1. The experimental result showed that the materials with the highest activity have the lowest ΔE , and ΔE values correlate well with the binding energy of oxygen which coordinates to metal ions.

The phenomena of conductivity change during sensing function can be explained by the following equations, when the reducing gas is adsorbed on, e.g., p-type LaMO₃ (M = Mn Cr, Co), ^[56]

 $CO(g) + O^{2-}(s) \rightarrow CO_2(s) + 2 e^{-s}$

 $H_2(g) + O^{2-}(s) \rightarrow H_2O(s) + 2e^{-}$



Fig. 2.3.1c. The change of electric conductivity of $SmCoO_3$ with time after injection of CH₃OH at 513 K. The carrier gas was N₂ containing ca. 50 ppm O₂ at a flow rate of $40cm^3/min^{[53]}$.

Table 2.3.1. Apparent activation energy ΔE values for various perovskite-type oxides.^[54]

Compound	$\Delta E (eV)$	Compound	$\Delta E (eV)$	
LaCoO ₃	0.14	LaCrO ₃	0.28	
AmCoO ₃	0.13	SmCrO ₃	0.22	
EuCoO ₃	0.09	EuCrO ₃	014	
LaMnO ₃	0.25	LaFeO ₃	0.98	
SmMnO ₃	0.25	NdFeO ₃	0.74	
EuMnO ₃	0.27	SmReO ₃	0.55	<u></u>

 $CH_3OH (g) + 3O^{2-} (s) \rightarrow CO_2 + 2H_2O (s) + 6e^{-1}$

where (s) denotes a surface species and (g) denotes a gaseous species. As electrons are released upon adsorption, it enters the valence band resulting in the loss of a p-type conductivity hole. Therefore, the conductivity decreased. These equations mean that the catalytic reaction occurs on the surface of perovskite oxides.

d. Perovskite oxides SrFeO_{2.5+x} (O<x<0.5) as gas sensor materials

Nonstoichiometric perovskites $SrFeO_{2.5+x}$ (O<x<0.5) exist at temperatures of a few hundred degrees Celsius. Over this composition range there are a series of phases

derived from the perovskite structure. The structures of these phases can be considered as distortions arising from ordering of oxygen vacancies in the cubic lattice of SrFeO₃. The phase changes as the content of oxygen changes. The structure changes from the cubic perovskite at $x \approx 0.5$; to tetragonal at $x \approx 0.35$; to orthorhombic at $x \approx 0.25$ and to the brownmillerite structure at $x \approx 0$. These phases can be represented as a repeating sequence of octahedral and tetrahedral layers. They have recently been prepared electrochemically at room temperature and their structures were characterized in situ^[57]. $SrFeO_{2.5+x}$ are normally prepared and operated at high temperatures. The mobility of oxygen along defects is several orders of magnitude greater than in an ordered crystal. The defects responsible for the increased mobility are the stacking faults in the repeating sequence of octahedral and tetrahedral layers. Rapid mobility of the oxygen anions (or vacancies) along the stacking faults would be followed by diffusion over very small distances within ordered domains, on the order of several nanometers. Thus, the overall process is accelerated as a result of high diffusion coefficients over long distance and small diffusion coefficients over short distances.

The properties of SrFeO_{2.5+x} show different behavior, compared with other perovskite materials, e.g., SrFeO₃ deposited on Al₂O₃ at 200-400°C showed a conductivity increase when exposed to NO and a conductivity decrease to $CO^{[58]}$, while SrTiO₃ prepared by argon ion sputtering indicated an *n* to *p* type transition at oxygen partial pressures of 10⁻³-10⁻⁴ at 800-1000°C ^[59]. The limitation for practical uses of gas sensors is the stability of the perovskite phase in reducing atmospheres at high temperatures. Nakamura *etc* ^[60] investigated the stability of a series of perovskite–type oxides LaBO₃ (B = V, Cr, Mn, Fe,

Co, Ni) at 1000°C in gas mixtures of CO₂/H₂. The sequence of stability of these oxides was found to be LaCrO₃ > LaVO₃ > LaFeO₃ > LaMnO₃ > LaCoO₃ > LaNiO₃.

2.3.2. Perovskite oxides as catalyst materials

a. Perovskite materials as catalysts for the reduction of engine exhaust gas

Perovskite materials have been found as catalysts for the treatment of automotive exhaust. The principle of perovskites as catalysts for reduction of engine exhaust gas is that the B ions may be catalytically active 3d, 4d or 5d transition metal ions which occupy oxygen octahedrons. These octahedrons share corners in a cubic array. The A ions, which fit in to the dodecahedral interstices may be large rare-earth, alkaline-earth, alkali or other large ions such as Bi^{3+} or Pb^{2+} (Table 2.3.2). The diverse properties of the perovskites are derived on the one hand from the large variety of A and B ions which fit the structure and on the other hand from the variation in the valence state of the transition metal ions which can be obtained by proper choice of the A ions. Solid solutions of ABO₃ with A'BO₃, AB'O₃ or even A'B'O₃ (A' and B' signify substitution to the A side and B site, respectively) enhance capability for specific properties. Pb and S are catalyst poisons derived from the fuel and their compounds produced in the combustion process. Perovskite catalysts have particular promise, because Pb is a common component in the ABO₃ formula and is not a chemical poison for these catalysts. Although perovskite catalysts, like other oxide catalysts, can be poisoned by S that occurs naturally in the petroleum products used as fuel, a small amount of Pt in the perovskites can significantly improve their poisoning resistance.^[61, 62]

Dodecahedral A site			Octahedral B site		
Ion	Radius (nm)*	Radius(nm)**	Ion	Radius(nm)*	radius(nm)**
Na ⁺	0.106	0.132?(IX)	Li ⁺	0.068	0.074
\mathbf{K}^{+}	0.145	0.160	Cu ²⁺	0.072	0.073
Rb⁺	0.161	0.173	Mg ²⁺	0.066	0.072
Ag ⁺	0.140	0.130(VIII)	Zn^{2+}	0.074	0.075
Ca ²⁺	0.108	0.135	Ti^{2+}	0.076	0.067
Sr ²⁺	0.123	0.144	V^{2+}	0.074	0.064
Ba ²⁺	0.146	0.160	Cr ³⁺	0.070	0.062
Pb^{2+}	0.129	0.149	Mn ³⁺	0.066	0.065
La ³⁺	0.122	0.132?	Fe ³⁺	0.064	0.064
Pr^{3+}	0.110	0.114(VIII)	Co^{3+} (LS)		0.052
Nd ³⁺	0.109	0.112(VIII)	Co^{3+} (HS)	0.063	0.061
Bi ³⁺	0.107	0.111(VIII)	Ni^{3+} (LS)		0.056
Ce ⁴⁺	0.102	0.097(VIII)	Ni^{3+} (HS)	0.062	0.060
Th ⁴⁺	0.109	0.104(VIII)	$ Rh^{3+} $	0.068	0.066
			Ti^{4+}	0.068	0.060
			Mn^{4+}	0.056	0.054
			Ru ⁴⁺	0.067	0.062
			Pt ⁴⁺	0.065	0.063
			Nb ⁵⁺	0.069	0.064
			Ta ⁵⁺	0.069	0.064
			Mo ⁵⁺	0.062	0.060
			W ⁶⁺	0.062	0.060

Table2.3.2. Cations commonly found in perovskite-type oxides. In parentheses is the coordination number if the radii given are not for 12 coordinations; HS and LS refer to high spin and low spin, respectively.

* From^[63] ** From^[64]

b.. Perovskite materials as electrolyte and electrodes in electrocatalytic fuel cell

A solid oxide fuel cell (SOFC) is an all solid-state energy conversion device that produces electricity by electrochemically combining fuel and oxidant gases across an ionic conducting oxide. Current SOFC use an oxygen-ion conductor or a proton conductor as the electrolyte and operate at high temperatures (>600°C). SOFCs are presently under development for a variety of power generation applications. The science and technology of ceramic fuel cells have been reviewed by Minh. ^[65] One of the critical

issues posed by the development of this type of fuel cell is the component materials, the examples are ZrO₂ as electrolyte, nickel/ZrO₂ cermet anode, LaMnO₃ cathode, and LaCrO₃ interconnect. Currently, one of the goals in SOFCs development is to decrease the operating temperatures. Decreased operating temperature can effectively increase the reliability and decrease the cost of the fuels ^[66]. For this purpose, some perovskites such as strontium--doped LaMnO₃ coated with yttria-stabilized zirconia thin film is a general material used as a solid electrolyte in SOFCs.^[67] However, the challenge will still be met in other respects such as the oxygen-ion conductivity.^[68] Another example is La_xSr₁. _xMnO₃ powders that are widely used as air electrode materials in SOFCs and therefore are directly related to the efficiency of the system.

2.4. Kinetic phenomena in thin film couples

The value of a material relies not only on the potential of its applications, but also, most importantly on its properties utilization which is realized in functional devices. In many case these devices are made through thin film deposition. Consequently the field of thin film deposition has caused intensive interest from manufacturers and researches for decades, where the kinetic phenomena in terms of solid state amorphization, diffusion in thin film couples and interfacial reactions during thin film deposition and post heat treatment occur. From materials characterization point of view, review in this field will help understand the interfacial reactions that occur in the SrFeO₃ /SiO₂/Si thin films systems to be studied.

2.4.1. Solid state amorphization in thin films

Amorphization has been found in many thin films to Si and III-V semiconductor substrate systems, including metalization on single crystal Si, GaAs and InP or ceramics thin film to these semiconductor substrates, such as Ti-Si ^[69, 73], Ni-Si ^[74], Ti-InP^[75], Ni-InP^[76] and SrFeO₃-Si ^[77]. A very thin amorphous layer is formed during the thin film deposition at relatively low or at room temperature. When these thin film system are annealed, the amorphous phase develops or disappears depending on the annealing temperatures, and one or more crystalline phases form. More extensive research on solid state amorphization reactions has been done in metal-metal systems than in thin films-semiconductor systems so that the theoretical and experimental results from metal-metal systems are often used to explain phenomena observed in thin film-semiconductor systems. These results are briefly summarized in the following ^[78, 79]:

(1) Amorphous, as a result of interfacial reaction or direct deposition, appears as layer at the interface.

(2) Solid state amorphization results in amorphous alloy due to a lower free energy than that of the bilayer structure (i.e., two metals separated by an interface).

(3) Amorphous growth rate is constant in time at the initial stage of the reaction and parabolic during the latter stages. The atom transportation over the growing layer plays the dominant role in controlling the amorphous growth ^[78, 79].

(4) Diffusivities of elements in a thin film couple are different. The elements with high diffusivities are the major diffusers in the growing amorphous layer.

(5) Formation of an amorphous (metastable) phase other than any stable crystalline phases in a given thin film system is due to kinetic constraints on crystalline phase

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nucleation^[78]. The suggested possible kinetic constraints^[80] are (a) absence of mobility of one component, such as refractory metal atoms in a near noble metal-refractory metal couple; (b) "kinetic interfacial barrier", in the other words, the absence of a low energy or coherent interface between the intermetallic crystalline compound and the parent metals of the diffusion couple. This is because the successive atomic rearrangements required for growing an intermetallic compound from an existing interface may require many correlated atomic jumps, which would lead to a small interfacial mobility. Experimental support for the original interface between two metals and the grain boundaries to act as preferred nucleation sites of amorphization has been obtained.

The study ^[81] of thermodynamic stability of metal amorphous oxide film on its metal substrate showed that amorphous structure for an oxide film on its metal substrate can be more stable than the crystalline structure. The thermodynamic stability of a thin amorphous metal-oxide film on top of its single-crystal metal substrate has been modeled and the estimation of the interface energies of the metal (substrate) /amorphous-oxide film and the metal (substrate)/ oxide film (crystalline-oxide) have been described as a function of growth temperature, and crystallographic orientation of the substrate (including the effect of strain due to the lattice mismatch). The energy of the interface between a crystalline oxide. For sufficiently thin oxide films on a metal substrate , the amorphous state can be preferred over the crystalline state, because the higher bulk energy of the amorphous oxide film, as compared to the corresponding crystalline oxide film, can be overcompensated for by the relatively low sum of the amorphous-oxide film

surface energy and metal (crystal)/metal oxide (amorphous) interfacial energy. The differences in the relative stability of an amorphous oxide film on different crystallographic faces of the metal substrate are caused by the differences in the crystalline –crystalline interfacial energy. Formation of a crystalline oxide is more likely for a more densely packed crystallographic face of the metal substrate.

In metal-Si systems, it is found that some experimental results are very similar to those observed from metal-metal couples. Gibbs free energy versus composition and metastable phase diagrams for the Ti-Si system have been calculated ^[80] which show that there is a large negative heat of mixing of the components in this system and that amorphous phase formation is possible over a wide composition range. Based on the magnitude of the calculated values, these systems are divided into two categories ^[82], i.e., those with large negative mixing enthalpy values, in which amorphization is favorable and those with small negative mixing enthalpy values, in which amorphization is unfavorable. Experimental results from the literature do not agree very well with this classification ^[82-92]. It seems that a negative mixing enthalpy is a necessary condition for solid state amorphization, but cannot be taken as a criterion.

Fast diffusion of one component in the amorphous phase may be an important condition of solid state amorphization in metal-Si systems. The reaction kinetics for solid state amorphization is about five orders of magnitude faster than that for crystalline silicide formation at the same temperature ^[70] which implies Si diffusion is much faster in the amorphous layer than in the crystalline silicide layer. In addition, it usually occurs in metal- metal systems and very common in almost all metal-Si systems when annealed at

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relative low temperatures that one of the two components of a given diffusion couple diffuses much faster than the other. In this case, solid state amorphization behavior exhibit and this is believed to be one of possible kinetic constraints for crystalline phase nucleation ^[78]. However, this type of diffusion only a necessary condition rather than a sufficient condition for solid state amorphization to occur, because it has not been proved to be universally applied ^[71, 73, 82, 86]. In consequence, the essential factors permitting amorphization are fast diffusion of one component and the existence of a negative value of mixing enthalpy in the binary system ^[82, 84]. It is believed that the reason for solid state amorphization to occur is due to kinetic constraints on crystalline phase nucleation ^[78, 80].

2.4.2. Reactions during thin film deposition

a. Direct deposition reactions: Reactions between the deposited films and substrates during thin film deposition are usually called direct deposition reactions. In the case of metal/Si system, the reaction takes place readily even at room temperature, when the first few layers of metal atoms are deposited onto the Si substrate ^[86-99]. It is found that, in Ni-Si and Co-Si systems, the first silicide formed during deposition is different from that observed during thermal annealing of thin film couples ^[88-95]. In other systems, however, such as the Pd-Si ^[86, 88, 98, 99] and Fe-Si ^[100,101] systems, initial silicides are the same for direct deposition reaction and thermal reaction of thin film couples in a given system. These phenomena cannot be explained by existing theories for silicide formation, or by other theories for solid state reactions.

Reaction during deposition in thin film is explained based on the fact that when deposited

species in vapor phase condense on a surface, latent beat (which basically is the difference in potential energy between vapor phase and solid phase) will be released. This energy is usually on the order of a few electron volts per atom. If this energy is directly transferred to one or two Si atoms as soon as a deposited atom reaches the Si surface, it is large enough to allow the Si atom(s) to break its (their) chemical bonds with the Si substrate and react with the deposited atoms readily without the help of thermal activation.

b. Sequence of direct deposition reactions: Phase formation sequence between thin film and substrate has drawn a lot of attention. It is found that the thickness of the film plays a significant role in the phase formation sequence. Many experimental results show that epitaxial NiSi₂ forms on (111) Si substrates during deposition at room temperature if the Ni thickness is less than three monolayers ^[88, 91, 94, 95]. When the Ni thickness is between 3 and 10 monolayers, either Ni islands or NiSi₂ islands topped by some unreacted Ni are observed ^[96]. Above 10 monolayers of Ni, the silicide islands coalesce, the Ni-Si reaction stops, and unreacted Ni starts to accumulate on top of the reacted layer.

c. Temperature dependence of deposition reaction sequence: Deposition temperature also plays an important role in phase formation sequence. In the Pt-Si system, the initial phase that formed during deposition at room temperature was reported to be polycrystalline Pt_2Si ^[86] and an amorphous phase with a composition close to either Pt_2Si or PtSi. An earlier study provides evidence that Pt_2Si forms initially at 320°C while PtSi forms first at 400°C during deposition. ^[94] It is observed ^[96] that when 5 monolayers of Fe are deposited onto (100) Si substrates at room temperature, the interaction between Fe and Si produces a polycrystalline or an amorphous FeSi silicide film of 3 monolayer

thick. This silicide film is uniform and homogeneous. There is some unreacted Fe lying on top of the FeSi film. According to the study, ^[97] by selecting an adequate temperature range, it is possible to directly grow a certain phase on the Si substrate. Their results show that when a fixed deposition rate is used, epitaxial FeSi and β -FeSi₂ can form as the initial phase when the Si substrate is held at 475°C and 750°C, respectively. This is attributed to the different diffusivities of Si at those temperatures.

d. Other factors affecting the sequence of deposition reactions: Deposition rate, deposition method, the type of materials to be deposited, and substrate temperature are be the main factors that determine formation sequences during deposition considering that energy is transferred by the metal atom to the Si atoms surrounding in the lattice causing increase of temperature in the local crystal lattice, therefore, the Si atoms are in a thermally activated state. The effects of these factors on the reaction could be quite complex, e.g., faster deposition rates will inject more power (i.e., energy per unit time) into the substrate surface area, which may accelerate the reaction if the reaction is fast enough to consume the deposited species. On the other hand, faster deposition rate means faster supply of deposited species to the surface. Kinetically unfavorable situation occur if the reaction rate for a certain compound formation is not as fast as the supply rate of the deposited species. This inference is in agreement with the result that a small deposition rate in the range of a monolayer per minute favors the room temperature growth of epitaxial CoSi₂^[98, 99]. These phenomena are well explained using the kinetic model ^[100] describing phase formation sequence, especially the first phase formation during direct deposition reactions.

2.4.3. Diffusion in thin film couples

Identification of the major diffuser, diffusivity of the moving species in the growing phase, and the effects of crystalline defects on diffusion are of most interest in study of thin film couples. Special aspects of diffusion in thin films have been reviewed ^[101, 102].

a. Identification of the major diffuser: Identification of the major diffuser is very important in explaining the complicated phenomena in thin film reactions. The major diffusers in most transition metal silicides are well documented. Table 2.4.3a shows a summary of major diffusers determined from marker experiments ^[103-112]. According to these articles, in many disilicides the majority atoms constitute a continuous network on which a vacancy can easily migrate. On the contrary, the motion of minority atoms requires either the coexistence of two vacancies (minority and majority) or a local destruction of the crystalline lattice. In either case the motion of the minority atoms will be characterized by activation energy considerably larger than that for the majority atoms. For monosilicides, such as NiSi, CoSi, PtSi, FeSi, IrSi, etc., there is no general rule for major diffusers. Even the silicides which are isostructural compounds may have different moving species. As an example, NiSi, FeSi and IrSi all have the FeSi-B20 structure, but, from Table 2.4.3a, metal atoms are the moving species in NiSi while Si is the major diffuser in FeSi and IrSi. For some silicides, such as CoSi, PtSi and PdSi the identity of moving species is still controversial. Investigations suggest that Co^[105] is the major diffuser in CoSi and Si^[109] is the moving species in PtSi. Earlier experiments show that both Si and Pd diffuse during PdSi formation. The result from the study ^[110] indicates that Si is the dominant diffuser while Pd will participate in mass transport only when Si

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motion becomes obstructed.

1 4010 2.4.	a. Major unit	sets in unit sine			
Silicide	Diffuser	Marker	Silicide	Diffuscr	Marker
TiSi ₂	Si	Xe, Si	RhSi	Si	Ar
V ₃ Si	V	Xe	Rh ₄ Si ₅	Si	d
VSi ₂	Si	Xe, c	Rh ₃ Si ₄	Si	d
CrSi ₂	Si	Xe, Si	Pd ₂ Si	Pd and Si	0, W
FeSi	Si	Xe	PdSi	Pd and Si	W
Co ₂ Si	Co	W, Si, Xe	TbSi _{1.7}	Si	c, Kr, Ar
CoSi	Si, Co	Ta	ErSi _{1.7}	Si	c, Kr, Ar
CoSi ₂	Si, Co		HfSi	Si	Zr, Ar
Ni ₂ Si	Ni	Xe, Si	TaSi ₂	Si	Nb
NiSi	Ni	Xe	WSi ₂	Si	C, Mo, Ge
NiSi ₂	Ni	Xe	Os ₂ Si ₃	Si	С
YSi _{1.7}	Si	Tb, Er, Kr	IrSi	Si	Co. Rh
ZrSi ₂	Si	Si	IrSi _{1.75}	Si	Co, Rh
NbSi ₂	Si	c, V	Pt ₂ Si	Pt	Si
MoSi ₂	Si	С	PtSi	Pt, Si	Pt, Si
RhSi ₃	Si	W			

Table 2.4.3a. Major diffusers in thin silicide films^[110-112]

c: By analogy from isomorphous silicide studied in the same investigation.

d: Deduced from oxidation experiments.

b. Determination of diffusivity of moving species: Diffusivity of the moving species in the growing phase is essential for kinetic studies. For example, in the competitive growth model ^[113, 114] diffusivity and the effective interface reaction barrier are crucial kinetic factors in determining whether a phase can grow. Data for diffusion activation energies have been reported (Table 2.4.3b). Diffusivity usually is experimentally determined. The diffusivities and activation energies are also determined from concentration profiles in the phases under consideration. ^[115]

c. Defects behavior in reaction kinetics: (1) Surface vacancies support reaction: it is found that when metal contacts of TiPdAg, MgPdAg, and NiAg to Si are capped with

 Ta_5O_2 the thermal reactions between the metals and Si are either suppressed or enhanced, depending on the contact system ^[116]. This is because the capping layer suppresses both the generation and annihilation of vacancies at the free surface of the metal which are necessary to support the reactions. Since a self diffusion coefficient measured from a bulk sample is not necessarily the same as that in a thin film sample of the same material, the diffusion study can be complicated significantly by the presence of a high density of defects. The high density of vacancies in the thin film will result in a smaller activation energy or larger diffusivity for self diffusion. During thermal reaction, the vacancies are annihilated faster than they are generated; the diffusivity will decrease with annealing time. Diffusivity change of the major diffuser in the growing layer will, as a result, affects the reaction kinetics. (2) Solid state reactions in thin film take place at interface: the solid state reactions take place only at the interfaces between various phases. From this point of view, knowing the major diffuser, its flux at a given interface and the composition of the growing phase at this interface is enough to study the effects of diffusion on interface reaction kinetics. A simple method for determining the difference in diffusion fluxes, ΔJ ($\Delta J = J_{in}-J_{out}$, where J_{in} and J_{out} are the fluxes into and out of the interface under consideration) at reactive interfaces has been developed [117]. The primary advantage of this method is it allows the diffusion flux, J, to be estimated without knowing the information about diffusivities, concentration or chemical potential gradients, defect densities, and the change of diffusivities with concentrations and defect densities, etc. In addition, by linking the diffusion flux at a given time with the phase that is growing at the interface at the same time, the relation between diffusion and formation sequences of products of interfacial reaction is made evident.

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Metal	Silicide	E _A (eV/atom)	Reference	Comments
Hf	HfSi	2.5	[3]	
	HfSi ₂	3.5	[97]	on amorphous Si
W	W ₅ Si ₃	3.7	[104]	<u> </u>
	WSi ₂	2.2, 3.0	[3, 104]	
Ir	IrSi	1.9	[3, 4]	
Pt	Pt ₂ Si	1.3, 1.5	[3, 4, 35]	
	PtSi	1.5, 1.6	[3, 4, 35]	(on Si (100), Si (111))
Ti	TiSi	1.8	[4]	
	TiSi ₂	1.8	[72]	
V	V ₃ Si	2.0	[104]	
	VSi ₂	1.7	[104]	
Cr	CrSi ₂	2.3	[79]	
Mn	MnSi	1.3, 1.9	[7, 41, 53]	
Fe	FeSi	1.36	[83]	
	β-FeSi ₂	2.6	[83]	
Со	Co ₂ Si	1.5	[4]	(bulk couple)
	CoSi	1.9, (1.66)	[4], [(122)]	(bulk couple)
	CoSi ₂	1.97	[123]	bulk couple
Ni	Ni ₂ Si	1.5, (1.3)	[3], [(37)]	(on polycrystal Si)
		1.5, (1.6)	[37]	on Si(100), (Si(111))
	NiSi	1.4-1.65	[3]	
		1.23, (1.83)	[95]	on Si (100), (Si(111))
Mo	Mo ₃ Si	3.3	[104]	
	Mo ₅ Si ₃	3.7	[104]	
	MoSi ₂	2.2, 2.4	[4, 100, 104]	
Rh	RhSi	1.95	[3]	
Pd	Pd ₂ Si	0.9	[103]	on amorphous Si
		0.95, (1.05)	[103]	on Si (100), (Si (111))

Table 2.4.3b. Apparent activation energy for selected elements.

2.5. Stability of perovskite thin film systems

Stability of perovskite thin film systems has attracted strong interest in the field of device applications. The purpose of the studies is to ensuring the extraordinary properties of the perovskite materials in its applications. Studies show that the stability of perovskite systems is affected by temperature and duration of heat treatment, orientations as well as surface condition of the substrates.

2.5.1. Temperature effect

The La_{2/3-x}Li_{3x} $\Box_{1/3-2x}$ TiO₃ (3x=0.3, \Box : an additional element) thin film (LLT), as a new electrolyte for solid-state microbatteries, were widely investigated. In which, the stability of the interface between the perovskite material and the cathodes is concerned during the thin film fabrication.^[118-122] The as-deposited LLT films exhibit amorphous structure, while as-deposited cathodes exhibit poor crystallinity, [118,121,122] therefore, LLT and cathode films have to undergo a thermal treatment to enhance their crystallinities and properties. The stability of the system is critical since reactions at the interface of the electrolyte and cathode during the thermal treatment would affect the properties of the microbatteries. Interfacial reactions between LLT and the common-used cathodes LiNiO₂, LiCoO₂ and LiMn₂O₄ were investigated.^[123] Phases identified by x-ray diffraction on the mixtures of the electrolyte and cathode powders after thermal treatments at different temperatures showed that the stability of $LiMn_2O_4$ / LLT system was well demonstrated after thermal treatment at as high as 800°C. LiCoO₂ /LLT system remained stable at 700°C, but a β -LLT phase was observed after 800°C annealing. The LiNiO₂ / LLT system showed poor stability due to decomposition of LiNiO₂ and LLT forming NiO and La₂Ti₂O₇ after annealing at $T > 500^{\circ}$ C. Thus, the conductivity decreased as a result of the decomposition. Another example is that in an observation on the thermal stability of the (1-x)Pb(Zn_{1/3}Nb_{2/3})O₃-xPbTiO₃ thin film system.^[124] The films with different compositions were annealed at different temperatures and durations. The bond valence method was used for analyzing perovskite structural stability. The bondvalence of a cation or anion in a crystal is determined by its coordination number and bond length between cations and anions, therefore, the stability of a crystal structure can be estimated. The result showed that the thermal stability of the $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ perovskite phase degraded with reducing of the PbTiO_3 amount and increasing of annealing temperature and duration. When the PbTiO_3 amount was low, the perovskite phase formed at a lower temperature was transformed into pyrochlore phase at an elevated temperature. An extended annealing duration also favored the transformation form perovskite to pyrochlore.

2.5.2. Elemental concentration effect

Elemental concentration is a sensitive factor affecting the stability of perovskites. Except for the $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$ -xPbTiO₃ perovskite, where PbTiO₃ concentration is a factor affecting the stability of the perovskite, perovskite $La_{2/3-x}Li_{3x}\Box_{1/3-2x}TiO_3$ has been investigated as a new electrolyte for solid-state microbatteries for the last few decades, due to its high lithium-ion conductivity (~10⁻³ SCm⁻¹).^[125, 126] It was reported that the lithium-ion conductivity is strongly related to and varies with the concentrations of lithium-ion and A site vacancies. The study^[127] on Sr(Ti_{1-x}Ru_x)O₃ (STRO) epitaxial thin films deposited on single-crystal SrTiO₃(100) showed that thermodynamic stability increase with the decrease of Ru concentration, and STRO (x<0.50) is free from degradation under annealing at 600°C in H₂ atmosphere, indicating its high resistance against reduction process when Ru in this peroskite is low (x<0.5).

2.5.3. Substrate effect

Perovskite phase stability of $0.67Pb(Mg_{1/3}Nb_{2/3})O_3-0.33PbTiO_3$ epitaxial thin films by deposition onto miscut substrate was reported. ^[128, 129] Films were grown on (001) SrTiO_3

substrates with miscut angles form 0 to 8° toward the [100] direction using 90° off-axis magnetron sputtering. Films on high miscut substrate (> 4°) were identified to be a nearly stoichiometric perovskite phase by both x-ray diffraction and TEM imaging. In contrast, films on exact (001) SrTiO₃ contained a high volume fraction of pyrochlore phase with Pb deficiency. Films on 8° miscut substrates have much smoother surface morphology than those on the SrTiO₃ with the exact (001) orientation, where the pyrochlore phases nucleated on top of the perovsitite phase, and the amount of the pyrochlore phase increases with film thickness.

The influences of lattice mismatch between thin film $Ca_2Fe_2O_5$ and different substrates on the structure of the $Ca_2Fe_2O_5$ thin films have been investigated.^[130] The $Ca_2Fe_2O_5$ films were deposited by pulsed laser deposition on (001)-oriented SrTiO₃, LaAlO₃, and (LaAlO₃)_{0.3}(SrAl_{0.5}Ta_{0.5}O₃)_{0.7} substrates respectively. The study shows that minor variations in the lattice mismatch of the $Ca_2Fe_2O_5$ film with the three different substrates determine the growth direction of the film. The misfit stress produced by the lattice mismatch promotes the development of strain accommodation mechanisms in order to minimize the free strain energy. As a result, (101) "orthogonal" twins are formed to accommodate the misfit in the epitaxial films of $Ca_2Fe_2O_5$ on SrTiO₃(001) and (LaAlO₃)_{0.3}(SrAl_{0.5}Ta_{0.5}O₃)_{0.7} (001), while $Ca_2Fe_2O_5$ films on LaAlO₃ (001) develop 90° rotation twins leading to film fragmentation into grains. The formation of $Ca_3Fe_2O_7$ in the $Ca_2Fe_2O_5$ thin films on SrTiO₃ and (LaAlO₃)_{0.3}(SrAl_{0.5}Ta_{0.5}O₃)_{0.7} leads to a change in the chemistry of the film in addition to the structure.

Chapter 3

Experimental methodology

Generally, information about materials needed for characterization includes the crystal structure, the crystal defects and the surface structure. The number, size, shape and distribution of the crystalline particles are of interest for polycrystalline solids powders or ceramics. A variety of techniques have to be used in combination for a complex characterization. There are three main categories of physical techniques, which may be used to characterize solids organic or inorganic materials: (a) diffraction, (b) spectroscopic, and (c) microscopic techniques. Proper technology chosen in materials characterization is critical. The principle of these technologies is described in the following sections. Diffraction techniques including x-ray diffraction, electronic diffraction and neutron diffraction are briefly described in section 3.11, 3.1.2 and 3.1.3 respectively. In section 3.1.4 emphases are made on the quantitative analysis of energy dispersive spectrometry (EDS). The principle of high resolution transmission electron microscopy is addressed in section 3.1.5. The reason why these techniques are emphasized is that these technique can be realized by using a analytical transmission electron microscopy (ATEM), which can take the advantage of high resolution imaging from TEM and combine the techniques of electron diffraction and spectrometry such as EDS and electron energy loss spectrometry (EELS) giving instant result about crystal morphology, structure, composition of material from a very small area of a specimen.

3.1. Principle of selected material characterization technologies

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3.1.1. X-ray diffraction

Crystal structure study using x-ray are based on the Bragg's law

$$n\lambda = 2d\sin\theta \tag{3.1}$$

where d is the interplanar d-spacing. θ is the angle of incidence, or Bragg angle, λ is the wave length of the incident x-ray beam. When the Bragg's law is satisfied the reflected beams are in phase and interfere constructively. At angles of incidence greater or smaller than the Bragg angle, reflected beams are out of phase and destructive interference or cancellation occurs.

Constructively interfered beams are present as peaks in x-ray spectra at certain angle representing the incident angles of the x-ray reflected from different crystal planes. The series of reflections with their intensities are unique for an individual material. Therefore it can be used to distinguish a material from others.

Powder x-ray diffraction has been used in almost all the characterization of perovskites, such as determination of crystal structure, structure defect and phase transformation^[131-133]. Shown in Fig, 3.1.1 is an x-ray spectrum of titanium carbide. A series of reflection peaks give their corresponding reflection angles, 2θ , which in turn can be interpreted as d-spacings using Brag's law. Since the diffraction pattern is unique for an individual material, thus an unknown material can be identified by comparing its x-ray diffraction pattern with the pattern of a known material available in its powder diffraction file (PDF). Thus the unknown material is determined. Peak intensity depends on the relative amount of the materials under irradiation. Therefore quantitative x-ray analysis

is possible to analyze the ratio of the elements in a material or the relative amount of a mixture of different materials. The intensity, width and position of the diffraction peak change with changes of the materials condition, such as crystal defects, internal stress, thickness of the film (for thin films) and particles size (for particles). For extreme small particles of a material, the intensity is low and the width of a peak is



Fig. 3.1.1.An x-ray diffraction pattern of titanium carbide (λ =0.15406nm).

widened. Therefore, in identification of crystal nature of nano-particles or nano-scaled substructure, this method has limited value, especially in the case of distinguishing between amorphous and nano-crystalline materials.

3.1.2. Electron diffraction

The principle of the electron diffraction (ED) is similar to x-ray diffraction. Techniques of ED include selected area electron diffraction (SAED) as well as related techniques, such as micro area electron diffraction (μ ED), weak beam electron diffraction and convergent beam electron diffraction (CBED). CBED pattern provides three dimensional information of the crystal structure. The unique advantage of CBED is that electrons interact strongly with matter and diffraction patterns are obtained from a very small area; so that it is the only reliable technique to be used to study very small samples. Unit cell point group, space group and crystal structure can be interpreted from CBED patterns.

Shown in Fig. 3.1.2 is a typical CBED pattern taken from a Si specimen. The pattern of the zero order Laue zone (ZOLZ) of a CBED pattern gives two-dimensional information about the lattice and the first order Laue zone (FOLZ) pattern is used to derive the third dimensional information about the lattice based on the equation:

$$R^* \approx (K_{\ell}^2 + 2H^*/\lambda)^{1/2} \tag{3.2}^{[134]}$$

where K_t is the component of the wave vector of the incident beam in the ZOLZ plane. K_t is used to specify the beam direction in CBED and $K_t = 0$ when the crystal is in zone axis orientation, R^* is the radius of a high order Lauer zone (HOLZ) reflection ring in the reciprocal lattice, H^* is the height of the corresponding HOLZ and λ is the electron wavelength. Both R^* and H^* are in reciprocal-space units (nm⁻¹). In practice, the value of H^* is obtained through the measured radius R (mm) of HOLZ reflection ring and the camera constant $L\lambda$ (mm nm)

$$H^* = \frac{R^2 \lambda}{2(L\lambda)^2} \tag{3.3}$$

Crystal structure determination using CBED also need the symmetrical analysis of the CBED which reflects the crystal symmetry information with characterized symmetric features ^[135-141].



Fig. 3.1.2. A typical micrograph of a CBED pattern from Si. The center pattern is the zero order Laue zone (also shown in the inset) providing two dimensional information of the crystal and symmetric information of the crystal and the out reflection ring is the first order Laue zone giving the third dimensional information of the crystal.

Electron diffraction techniques have been widely used in perovskite type materials. Long-range ordering and complexity of structure, such as characteristic of the existence of twins, the inhomogeneity of the arrangement of the structural features characterized with ED frequently occurred in the field of characterization of perovskite materials.

3.1.3. Neutron diffraction

In neutron diffraction a particular wavelength of neutrons are obtained from a nuclear reactor through a crystal monochromator. Neutron diffraction has been much used to locate light atoms, and to distinguish atoms that have similar x-ray scattering powers, such as Mn, Fe, Co and Ni. The neutron scattering powers of these atoms are different and for instance, superlattice phenomena, associated with Mn/Fe ordering in alloys, are readily observed by neutron diffraction.

Neutron diffraction is also a powerful technique for studying the magnetic structure of materials, for example, by x-ray diffraction NiO has the *fcc* rock salt structure. Neutron diffraction, however, showed extra peaks which indicated the presence of a



Fig. 3.1.3. Neutron powder diffraction patterns for MnO below and above the Néel temperature, T_N , together with a schematic x-ray powder pattern at room temperature. ($\lambda = 1.52$ Å).

superstructure. This arises because the unpaired d electrons (in the e_g orbitals) are

arranged so as to be antiparallel in alternate layers of nickel atoms ^[142]. Note that there is difference between the characteristic of neutron diffraction spectra and x-ray diffraction spectra. Fig. 3.1.3 shows neutron powder diffraction patterns for MnO below and above the Néel temperature, T_N , together with a schematic x-ray powder pattern at room temperature. In comparison of b and c, the peaks occur at same positions with very different intensities. In neutron pattern the small intensity of 200 and 220 in (b) is because the neutron scattering powers of Mn⁺² and O⁻² are opposite in sign. On the other hand, in the case with scattering of x-rays, for which the scattering factors of all elements have the same sign and therefore Mn⁺² and O⁻² scatter in phase with each other. Comparison of (a) and (b) shows that below T_N extra lines (asterisked) appear in the neutron diffraction pattern, these extra line are associated with the antiferromagnetic.

3.1.4. Energy dispersive x-ray spectrometry (EDS) analysis in TEM

An element in a specimen will generate characteristic x-rays when interaction with energetic electrons due to ionized atoms return to the ground state. As x-ray photons generated by inner-shell ionizations in the specimen enter the detector, a signal corresponding to the energy is processed into the appropriate channel of a multi-channel analyzer. As a result, the characteristic peaks appear in EDS spectra. Elements are identified by their characteristic peaks in the spectra. The characteristic peaks in EDS spectra are superimposed on a background which is due to Bremsstrahlung x-rays produced when electrons are slowed down by inelastic interaction with the nuclei in the specimen. Elements are identified by their characteristic peaks in the spectra. field of an atom. The electron decreases the magnitude of its velocity and its kinetic energy. The lost kinetic energy is emitted by the beam electron as a photon of electromagnetic radiation. This radiation is called bremsstrahlung which forms a continuous distribution of photon energies from zero up to the incident energy. The x-ray continuum is the principal component of the background of the x-rays spectrum from a thin foil.

Interface of the EDS with the AEM (analytical electron microscope) is shown in the Fig. 3.1.4. The major variables of concern are those of the detector (a) take off angle, α , (angle between the plan of the specimen and the detector axis) which can be changed by tilling specimen holder and is critical for x-ray absorption correction^[143]; (b) the solid



Fig. 3.1.4. The interface between the EDS and the AEM stage showing the desired collection angle Ω and the take- off angle.

angle of collection, which is commonly used by the approximation $\Omega \approx \frac{A}{S^2}$ (< 0.2)

steradians), where A = active area of detector, S = distance from specimen to detectorand (c) the resolution of the detector. Note that post specimen effects produce artifacts,which must be take into account especially in the case of analyzing thin specimen inTEM. Special artifacts such as escape peak, sum peak caused by operation at high beamenergy also should be paid more attention to.

An escape peak generates since a small faction of the energy is lost when the x-ray passes through the detector and not transformed into electron-hole pairs, resulting in a characteristic peak (escape peak) for an element in the specimen appearing in the spectrum. The escape peak occurs at an energy channel less than that of the element. The difference in energy between the escape peak and the characteristic peak of an element is equal to the lost energy. The often observed instance is that the incoming photon of energy *E* fluoresces a Si K α x-ray (energy 1.74 keV) which escapes from the intrinsic region of the detector. The detector then registers as energy of E-1.74 keV.

A sum peak arises when the electronic processing system is not fast enough. The conditions where this is likely to occur are the high input count rate and dead times. In this case, two photons could enter the detector at almost exactly the same time. The analyzer then registers an energy corresponding to the sum to the two photons, as a result, a sum peak appears in the spectrum.

In quantitative analysis, the first stage in the analysis of an unknown is the identification of elements present, a process referred to as qualitative analysis. Having obtained x-rays

from the desired regions of the specimen, the values of I_A and I_B can be converted to values of C_A and C_B by using either a ratio method or thin-film standard, where I_A and I_B are the intensities of the x-ray generated form element A and B in the specimen respectively; C_A and C_B are the concentrations of elements A and B in the specimen respectively. In both cases the determination of k factor is the key step to achieve quantitative result, where the k factor is the coefficient between, e.g., I_A and C_A .

Assuming in thin film electrons lose a small fraction of their energy and few electrons are backscattered and the trajectory of the electrons can be assumed to be the same as the thickness of the specimen film, t, the generated characteristic x-ray intensity,

$$I_{A}^{*} = const.C_{A}\omega_{A}Q_{A}\alpha_{A}t / A_{A}$$
3.4

where C_A = weight fraction of element A; ω_A = fluorescence yield (the fraction of ionizations that result in x-ray emission) for the K, L, or M characteristic x-ray line of interest; Q_A = ionization cross section, related to the probability of an electron of a given energy causing ionization of a particular K--,L-, or M-shell of atom A in the specimen; α_A = fraction of the total K, L, or M line intensity that is measured, and A_A = atomic weight of A.

If the analyzed film is so thin that the effects of x-ray absorption and fluorescence can be neglected, the generated x-ray intensity is identical to x-ray intensity leaving the film which can be measured and thus be called measured x-ray intensity. In reality, due to the absorption and fluorescence effects, the measured x-ray intensity is related to the

generated intensity by $I_A = I_A^* \varepsilon_A$, where ε_A is absorption and fluorescence related factor. *i.e.* $I_A = (const.C_A \omega_A Q_A \alpha_A t / A_A) \varepsilon_A = k_A^{-1} C_A$

If the x-ray intensities (I_A , I_B) of two elements A and B can be measured simultaneously, the procedure for obtaining the concentrations of elements A and B can be greatly simplified. And yield

$$\frac{C_A}{C_B} = \left[\frac{(Q\omega\alpha\varepsilon/A)_B\varepsilon_B}{(Q\omega\alpha\varepsilon/A)_A\varepsilon_A}\right]\frac{I_A}{I_B} = k_{AB}\frac{I_A}{I_B},$$
3.5

where
$$k_{AB} = \frac{(Q\omega\alpha\varepsilon / A)_B\varepsilon_B}{(Q\omega\alpha\varepsilon / A)_A\varepsilon_A}$$
, and $C_A + C_B = 1$

If a sample contains elements A, B and C (e.g., C is Si) and the k factors for A with C(Si) and B with C(Si), *i.e.* k_{ASi} and k_{BSi} (more common) are known, it is understood that

$$k_{AB} = \frac{k_{ASi}}{k_{BSi}} = \frac{k_A}{k_B}$$
 where k_A and k_B are $(Q\omega\alpha\varepsilon/A)_A^{-1}$ and $(Q\omega\alpha\varepsilon/A)_B^{-1}$ respectively.

In standards or experimental k factor approach, k factor can be plotted as a function of the K_{α} characteristic x-ray energy of various elements ^[144]. Metallurgists often display k factors as K_{AFe} factors because a large number of common metals can be alloyed in a convenient, homogeneous manner with the transition metals. Therefore, a k factor, such

as,
$$K_{AFe}$$
 can be obtained through $k_{AFe} = \frac{k_{AB}}{k_{FeB}}$.

Errors in quantitative electron microprobe analysis are caused mainly from the sources associated with specimen preparation, instrument operation, sampling, data collection and analysis. And experimental determination of k_{AB} requires many meticulous experiments,
so advantage of calculating k_{AB} is obvious by using the relation of $k_{AB} = \frac{(Q\omega\alpha\varepsilon/A)_B}{(Q\omega\alpha\varepsilon/A)_A}$,

Accurate values are difficult to compute because of the uncertainties in these fundamental parameters, but more accurate result could be reached if obtain all the terms needed to compute it.

Monte Carlo simulation of the effects of fast secondary electrons (FSE) on x-ray microanalysis in TEM, in which the effect of inelastic collisions of FSE is taken into account, showed that, except that the acceleration voltage of the primary electrons strongly affects k_{AB} factors, k_{AB} factors become dependent on the composition of a specific system of elements A and B and the thickness of the specimen analyzed^[145] in the case of A is a light element and B is a medium or heavy element. Parameterization under the effects of FSE as a function of specimen composition, specimen thickness and acceleration voltage of primary electrons on computing k_{AB} factor, as well as a guideline for developing an analytical strategy are presented^[146, 147]. On the other hand, the FSE degrade the spatial resolution.

Spatial resolution of EDS is a matter to consider in analytical electron microscopy (AEM) microanalysis. Spatial resolution is defined as the smallest distance, R, between two volumes from which independent x-ray microanalyses can be obtained. R is governed by the beam-specimen interaction volume, and described as $R = \frac{d + R_{\text{max}}}{2}$,

where R_{max} is given by $R = (b^2 + d^2)^{\frac{1}{2}}$ in which b and d are the beam size and beam

spreading respectively^[148].

3.1.5. High Resolution Electron Microscopy (HREM)

a. Electron wavelength

An electron can be referred to a wave. The wavelength λ of an electron wave is given by

$$\lambda = h / p = \frac{h}{\left[2m_0 eV \left(\frac{1 + eV}{2m_0 c^2}\right)\right]^{1/2}}$$
3.6

where *h* is Planck's constant, *p* is the momentum, *E* is the acceleration voltage of the electrons, and *e* and m_0 are the electron charge and mass. Relativistic effects is considered at energy above 100-keV.

The convenient approximate expression is

$$\lambda = (150/V)^{1/2}$$
 3.7

if the relativistic effects are ignored, for V in volts and λ in angstroms.

b. Resolution

For the classical incoherent imaging in light optics, the term resolution is judged by use of the Rayleigh criterion. An intensity distribution in the image from each point in the object plane is added. The points is called resolved if he corresponding maxima or minima of intensity in the image to the two points in the object can be distinguished as being separate. The minimum of the distance between two points that can be distinguished is thought the limit of the resolution

Resolution is described as

$$\delta = \frac{0.61\lambda}{\mu \sin \beta},$$
 3.8

55

where λ is the wavelength of the radiation, μ is the refractive index of the viewing medium, and β is the semiangle of collection of the magnifying lens. Rayleigh criterion is applied to the extent that imaging in the electron microscope can be approximated by an incoherent-imaging assumption, leading to what is usually referred to as the point-topoint resolution. The formula is approximated to $\delta = \frac{0.61\lambda}{\beta}$. Two measures of performance of an electron microscope have to be distinguished: the fineness of the detail that can be seen in an image and the amount of information that can be provided regarding the detailed structure of the object. This term is also applied on occasion to the more precise definition of resolution based on the assumption of the weak phase object and the Scherzer optimum defocus. Considering the effect of Cs^[149], the spherical aberration, and combining it with the Rayleigh criteria, the practical resolution of a microscope is described as

$$r_{\min} = 0.91 (C_s \lambda^3)^{1/4}$$
 3.9

c. Imaging geometry

Shown in Fig. 3.1.5a is a schematic system of a conventional TEM. In electron microscopes, electron beam from an electron gun through an illumination system of lenses (condenser lenses) illuminates the specimen and interacts with the specimen resulting in scattered radiation, which is then brought to a focus by the objective lens forming diffraction patterns (if specimen is crystalline) on the objective back focal plane and a image of the specimen on the selected area aperture plane. Then further magnifying lenses (intermediate lens and projective lens) produce an image of convenient size on the image plane.



Fig. 3.1.5a. The main elements of conventional TEM system.

Two important factors determine the essential geometry of the imaging system: the wavelength of the electrons and the aberrations of the lens. The wavelength of the electrons determines the angular range of the scattering from the specimen; the

aberrations of the electron lenses limit the angular range of scattered radiation that can usefully contribute to the image.

d. Imaging process

Fig. 3.1.5b suggests the basis for the production of an image following the wave-optics theory. A plane wave illuminates the specimen. The transmitted-wave function $\phi_1(xy)$ can be assumed to be composed of a forward-scattered, parallel transmitted wave plus other scattered waves that proceed in direction slightly inclined to it. The idea thin lens brings the parallel transmitted wave to a focus on the axis in the back focal plane.



Fig. 3.1.5b. Ray diagram suggesting the formation of a Fraunholfer diffraction pattern on the back focal plane of a lens and the subsequent formation of an image.

Waves leaving the specimen at the same angle ϕ_x with the axis are brought together at a point on the back focal plane, the waves from all parts of the specimen propagated in a given direction are added. So in this plane a diffraction pattern is formed, with maxima where waves from all parts of the specimen add constructively. The rays then form a common point in the object converge on a common point in the image plane. In practice due to lens defect and finite aperture the image is not a perfect reconstruction of the

object. The resolution of image detail is affected and the fine details of the intensity distribution may be distorted, i.e. a loss of resolution. An incident plane wave from all parts of the object are coherent and can interfere. The image amplitude is given by adding the amplitudes of the waves with their appropriate phase. For two image points close together, which have overlapping spread functions, the resultant intensity depends strongly on the relative phase of the waves at the two points. Fig. 3.1.5c indicates that the addition of amplitudes in images of two points sources and the resulting intensity distributions for the cases when the point source are in phase and out of phase.



Fig. 3.1.5c. Addition of amplitudes in images of two points sources and the resulting intensity distributions. (a) the point sources are in phase and (b) the point sources are out of phase.

e. Aberrations

Chromatic-aberration, spherical aberrations and astigmatism distort the wave fronts which cause loss of resolution. Chromatic-aberration due to incoherence of light source plays a role of incoherence on imaging. Spherical aberration is providing the most significant, cylindrically symmetrical perturbations of the phase change produced by a lens. In Fig. 3.1.5d, the geometric-optics and wave-optics representations of an imaging system with spherical aberration are compared. In geometric optics, paraxial rays are brought to a focus at the paraxial or Gaussian focus. Changes of the strength of the lens move this focus backward or forward by an amount Δf and so spread the image by amount $\Delta f \alpha$, where α is the angle the rays make with the axis. In the presence of thirdorder spherical aberration, the focal length decreases by an amount $C_s\alpha^2$ as α increases, where C_s is the spherical-aberration constant, so that the crossover at the paraxial-focus position is spread by an amount $Cs\alpha^3$. For a point source, the minimum beam diameter in the image space is not at the paraxial-focus position but at some distance closer to the lens. Hence, the best resolution in an image is obtained by defocusing (weakening) the lens to bring this minimum beam size into the image plane.



Fig. 3.1.5d. The effects of spherical aberration on the imaging of a point source in geometric optics. ^[150]

f. Image contrast

An image is seen because it has contrast. TEM images are classified as diffraction contrast images, mass thickness contrast images, Z contrast and phase contrast images based on the principle of image formation. The contrast are quantitatively defined as $C = (I_1 - I_2) / I_2 = \Delta I / I_2$, in terms of the difference in intensity between two adjacent areas. A

specific contrast technique could be used to obtain image with corresponding image for a specific purpose. In high resolution TEM, phase contrast is one of the most often used imaging concepts.

(1) Mass-thickness contrast

Mass-thickness contrast produced form incoherent elastic scatter of electrons is a strong function of the atomic number Z, as well as the thickness of the specimen. Images formed with electron scattered at low angles ($<5^{\circ}$) are mass-thickness dominated. However, within this angle it competes with diffraction contrast due to Bragg-diffraction. Mass-thickness contrast is most important concept in non-crystalline materials image analysis, because it is the only contrast mechanism applicable to these materials. Fig.3.1.5e



Fig.3.1.5e. Mechanism of mass-thickness contrast in a BF image.

schematically illustrates the mechanism of mass-thickness contrast in BF image without considering the diffraction effect. Thicker or higher-Z areas of the specimen (indicated by

the darker color) will scatter more electrons off axis than thinner of lower-mass (lighter colored) area. Thus fewer electrons from the darker region fall on the equivalent area of the image plane.

(2) Z contrast

The contrast formed by beams which contain only elemental information is called Z contrast. Z contrast is one of high-resolution (atomic) imaging techniques. It represents the limit of mass-thickness contrast where detectable scattering arises from single atoms or a column of atoms. Single atoms scatter incoherently and the image intensity is the sum of the individual atomic scattering contribution.

(3) Phase contrast and phase contrast images

Contrast in TEM images present due to differences in the phase of the electron waves scattered through a thin specimen is called phase contrast. Phase contrast can be exploited to image the atomic structure of thin specimens using TEM with sufficient resolution to detect contrast variations at atomic dimensions. A phase-contrast image requires the selection of more than one beam. The more beams collected, the higher the resolution of the image. If, for example, two beams are selected, *i.e.*, beam **0** and **g**, the interference of the two beams resulting in the intensity of the lattice fringes described as

 $I = A^2 + B^2 - 2ABsin(2\pi g'x - \pi st),$

where g' represents the magnitude of the diffraction vector \mathbf{g} ; s is excitation error and t is specimen thickness. A is relating to the direct beam amplitude and B is the function of the scattering through an angle corresponding to a change of diffraction vector \mathbf{g} . Thus, the intensity is a sinusoidal oscillation normal to g' and with a periodicity that depends on s and t. The intensity varies sinusoidally with different periodicities for different values of g'. With s = 0, fringes in the image have a periodicity in the x direction of 1/g, the spacing of the planes which give rise to g. With $s \neq 0$, the fringes will shift by an amount which depends on both the magnitude of s and value of t. In the many-beam case which is realized by aligning the beam parallel to a low index zone axis, images will appear as crossing lattice fringes or array of spots running in different directions. The lattice fringe images are best used as a measure of the local crystal structure and orientation but not direct images of the structure. An individual spot does not necessarily correspond to an atom in the real crystal.

g. HRTEM

High resolution images of an object rely on the TEM to transfer information from the specimen to the image. There are two obstacles to completely transfer the information from specimen, one is the imperfect optical system of the TEM resulting in image distortion and loss of information; the other is that atomistic model which includes a full description of the atomic potential and the bonding of the atoms for the material must be available to interpret the images.

High spatial frequencies correspond to large distances of scattered electrons form the optic axis. Therefore, the resolution in HRTEM is limited by the lens defect such as spherical aberration causing a spreading of the point in the image. As a result, the fine detail in the image is confused while the objective lens magnifies the image. Each point in the specimen plane is transformed into an extended region in the final image and each

point in the final images has contribution from many points in the specimen. In high resolution imaging, a linear relationship between the image and the weak specimen potential is needed so that it is import to know the nature of specimen and its reaction with electrons in a TEM system.

(1) Interaction of electron with specimens -phase change of electron wave

Since the scattering angles are small (~10⁻² rad), an electron wave traversing a thin specimen suffers a phase change that depends on the distribution of potential along a straight-line path through the object. Assuming function $\phi(xyz)$ represents the potential distribution in the object, when a plane wave transmitted through the object in the z-direction the phase change is a function of the x, y-coordinates, proportional to the projection of the potential in the z-direction: $\phi(xy) = \int \phi(xyz) dz$

The phase change of the electron wave, relative to a wave transmitted through a vacuum $(\phi=0)$, is given by the product of $\phi(xy)$ and an interaction constant σ (equal to $\pi/\lambda E$), which defines the strength of the interaction of electron waves with matter. Mathematically, the effect on an incident wave of the phase change is given by incident-wave amplitude transmission function: multiplying the by a $q(xy) = \exp[-i\sigma\phi(xy)]$, considering the effect of absorption which preventing some electrons form contributing to the image, the transmission function can be written as $g(xy) = \exp[-i\sigma\phi(xy) - \mu(xy)]$. The effect of this model is that, apart from $\mu(x,y)$, the specimen represents a "phase object" known as the pahse-object approximation (POA). This function emphasizes the nonlinear nature of electron scattering. Changes in the projected potential do not give proportionate change in the transmission function. The concept of a transmission function becomes invalid for thick specimens. For suitably thin g(xy) specimens, the wave function at the exit surface of the specimen can be described as a two-dimensional function $\phi_1(xy)$, which can be represented as the product of the incident-wave amplitude $\phi_0(xy)$ and the transmission function of the specimen g(xy). The exit wave has variations of phase and amplitude related to the specimen structure. Imaging process is then to produce a magnified representation of $\phi_1(xy)$ and to record an intensity distribution from which some information about the structure of the specimen can be derived. The thickness limitation of a specimens approximated as phase objects for fast electrons depends on the experimental conditions: for 100 keV electrons, for example, the thickness must be less than about 5nm if imaging with about 0.3nm resolution is being considered.

(2) Week-phase-object approximation (WPOA) and the transfer function

The transmission function of the specimen, or the image function g(xy), the impulse response function h(xy) and the specimen function $\phi(xy)$ can be represented by g(r), $h(\mathbf{r})$ and $\phi(\mathbf{r})$ respectively, where \mathbf{r} is the victor determined by the real spatial position of x, y in the specimen. In the reciprocal space, Fourier transforms of image function is related by

$$G(u) = H(u)\Phi(u) \tag{3.10}$$

where G(u) is the Fourier transform of g(r), the image function of point **r** in the specimen; $H(\mathbf{u})$ is the Fourier transform of $h(\mathbf{r})$, the impulse response function; $\Phi(u)$ is the Fourier transform of $\phi(\mathbf{r})$, the specimen function. Since h(r) describes how a information in real space is transferred from the specimen to the image, $H(\mathbf{u})$ is contrast transfer function. H(u) expressed by

65

where A(u) is the aperture function relating the cutoff signal with u spatial frequencies higher than some value governed by the diameter of the aperture.

 $E(\mathbf{u})$ is the envelop function, the property of the lens, describing the attenuation of the wave.

B(u) is the aberration function related to the over focus Δf and spherical aberration C_s , and u is the spatial frequencies.

Since coherent imaging is used in HRTEM, $B(u) = 2\sin \chi(u)$. T(u) is introduced and described as

$$T(\boldsymbol{u}) = A(\boldsymbol{u})E(\boldsymbol{u})2\sin\chi(\boldsymbol{u}), \qquad 3.12$$

where
$$\chi(\mathbf{u}) = \pi \Delta f \lambda u^2 + \frac{1}{2} \pi C_s \lambda^3 u^4$$
, 3.13

 Δf is known as overfocus, $\chi(\mathbf{u})$ is called phase-distortion function

T(u) is called transfer function. Only when the specimen acts as a weak-phase object, is the T(u) called the contrast transfer function. By ignoring E(u), the transfer function is described as

$$T(u) = 2A(u) \sin \chi(u)$$
 3.14

The phase –distortion function has the form of a phase shift expressed as $2 \pi / \lambda$ times the path difference traveled by those waves affected by spherical aberration (C_s), defocus, and astigmatism(C_a). If the astigmatism and the spherical aberration is corrected, the contrast transfer function is compared to the phase-distortion function, a number of observations can be made since the contrast transfer function is oscillatory. The transfer function shows maxima whenever the phase-distortion function assumes multiple odd values of $\pm \pi/2$. Zero contrast occurs for $\pm \pi$. In other words, when $T(\mathbf{u})$ is negative, atoms

would appear dark against a bright background, resulting in positive phase contrast; when T(u) is positive, atoms would appear bright against a dark background, resulting in negative phase contrast; when T(u) = 0, there is no detail in the image for the value of u. The ideal form of T(u) is a constant values as u increases, shown in Fig. 3.15f, meaning that information with a periodicity of spatial frequency corresponding to that value of u is strongly transmitted and appears in the image showing the same contrast, in terms of the atoms in a crystal appear as black or white spots. The large the u, the higher the frequency to which the information corresponds. u_1 defines the limit at which the image can be directly interpreted. When $u_1 > 0$ the contrast is reverses. Information at u_1 becomes complicated.



Fig. 3.1.5f. The ideal form of the transfer function.

In fact a point in a specimen is imaged as a disk since the $\chi(\mathbf{u})$ is a function of Δf and C_s . the radius of the disk is $\delta(\theta) = C_s \theta^3 + \Delta f \theta$. Fig3.1.5g. is a plot of $T(u)(=2\sin \chi)$ versus \mathbf{u} , drawn for certain value of C_s , E_0 (accelerating voltage) and, Δf . When \mathbf{u} is small the Δf dominates. χ repeatedly across the \mathbf{u} axis after the value \mathbf{u}_1 . Note that although χ is infinitely continuous but, in practice, it is affected by other factors and can be modified by the related functions, i.e., $T(\mathbf{u})_{\text{eff}} = T(\mathbf{u}) Ec Ea$, where chromatic aberration envelope function *Ec* and the spatial coherence envelope function *Ea* are called envelope damping



Fig. 3.1.5g. A plot of $T(\mathbf{u})$ versus \mathbf{u} (C_s = 1mm, E₀ = 200keV, Δf = -58nm).

functions. As a result, the χ plot stops, as shown in Figure 3.1.5h. At the first value of $T(\mathbf{u}) = 0$, \mathbf{u} is defined as point to point resolution and at the last is defined as information



Fig.3.1.5h. Aplot of $T(\mathbf{u})_{\text{eff}}$ versus **u**. Voltage: 200 keV Cs:1.2mm, Cc:1.2mm, Energy spread: 0.7eV, Convergence:0.25mrad, Focal Spread: 4.2 nm.

limit indicating that the microscope is incapable of imaging the finest details. Considering that χ is the function C_s and Δf , T(u) is strongly affected by these two parameters through sin χ . Fig. 3.1.5h shows a series of sin χ curves versus u when Δf or C_s is fixed. This implies that C_s and Δf are important factors in HRTEM imaging and atomic imaging is obtainable through improving C_s and selecting proper Δf . There is a particular negative value for which sin χ (**u**) has the most desirable form, a sharp negative peak, so isolated atoms or other features giving sharp maxima appear in the image as small, dark spots.



Fig. 3.1.5i. A series of sin χ curves calculated for different C_s in (a) and Δf in (b) ^[151].

Theoretically, the essential point about image formation of periodic objects is that their

diffraction patterns consist of sets of sharp spots, the diffracted beams. The beams are regularly spaced which represent distances in the back focal plane of the lens. The waves from this regular array of spots in the back focal plane then recombine to form periodic amplitude and intensity distributions in the image plane. The effect of the lens defocus and aberrations is then to change the relative phases of the finite set of regularly spaced diffraction spots. If the periodicity of the object is comparable to the resolution limit, the wave functions from adjoining unit cells overlap and interfere, giving an image intensity that is strongly affected by the periodicity. Correspondingly, in this case, the diffraction spots are well separated on the scale of the transfer function. So only a few points of the transfer function are relevant, and the modifications of the phases of the diffracted beams may depend strongly on the lattice spacing and the defocus. Thus, the imaging of periodic objects can represent special cases.

In practice, other factors besides the defocus and aberrations influence the formation of the images. So far the ideal case of a monochromatic plane wave incident on the specimen, *i.e.*, the case of perfectly coherent radiation has been assumed. For high-resolution electron microscopy of thin specimens, this assumption is a good approximation for most purposes, because the spread of the electron energies in the incident beam can be made very small. Also, the sources of electrons used have very small diameters and thus can be focused to give good approximations to incident plane waves. The more realistic situation is partially coherent radiation because the ideally coherent conditions cannot be achieved in practice, there are appreciable modifications of image detail at the current limits of resolution and the effective transfer function for weak

phase objects is modified.

3.2. Thin films preparation - Pulsed laser deposition (PLD) of thin films

Pulsed laser deposition (PLD) belongs to the category of physical vapor deposition, (PVD). It is a technique where a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the desired composition. Material is then vaporized from the target and deposited as a thin film on a substrate facing the target. This process can be realized in ultra high vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the deposited films (Fig. 3.2). When the laser pulse is absorbed by the target, energy is first converted to electronic excitation and then into thermal, chemical and mechanical energy resulting in evaporation, ablation, plasma formation and even exfoliation.^[152] The ejected species, containing many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten globules, expand into the surrounding vacuum in the form of a plume before depositing on the typically substrate.

The process of PLD can generally be divided into four stages: Laser ablation of the target material and creation of a plasma; dynamic of the plasma; deposition of the ablation material on the substrate and nucleation and growth of the film on the substrate surface.

(a) Laser ablation of the target material and creation of a plasma

The removal of atoms from the bulk material is done by vaporization of the bulk at the surface region in a state of non-equilibrium and is caused by a Coulomb explosion. The incident laser pulse penetrates into the surface of the material. This dimension of the penetration is dependent on the laser wavelength and the index of refraction of the target material at the applied laser wavelength and is typically in the region of 10 nm for most materials. The strong electrical field generated by the laser light is sufficiently strong to remove the electrons from the bulk material of the penetrated volume. The free electrons oscillate within the electromagnetic field of the laser light and can collide with the atoms of the bulk material thus transferring some of their energy to the lattice of the target material within the surface region. The surface of the target is thus heated up and the material is then vaporized. The temperature of the generated plasma plume is typically 10000 K.

(b) Dynamic of the plasma

In this stage the material expands in plasma parallel to the normal vector of the target surface towards the substrate due to Coulomb repulsion and recoil from the target surface. The spatial distribution of the plume is dependent on the background pressure inside the PLD chamber. The density of the plume can be described by a cosine law with a shape similar to a Gaussian curve. Increasing the background pressure results in slowing down of the high energetic species in the expanding plasma plume. Particles with kinetic energies around 50 eV can resputter the film already deposited on the substrate. This results in a lower deposition rate and can furthermore result in a change in the stoichiometry of the film.

(c) Deposition of the ablation material on the substrate

Deposition is the dominate stage determining the quality of the deposited films. The high energetic species ablated from the target are bombarding the substrate surface and may cause damage to the surface by sputtering off atoms from the surface but also by causing defect formation in the deposited film. The sputtered species form the substrate and the particles emitted from the target form a collision region, which serves as a source for condensation of particles. A thermal equilibrium can be reached when the condensation rate is high enough. and the film grows on the substrate surface through consuption of the direct flow of ablation particles.

(d) Nucleation and growth of the film on the substrate surface

Several factors influence the nucleation process and growth of crystalline film on a substrate, such as the density, energy, ionization degree of the ablated material and



Fig. 3.2. Schematic illustration of PLD configuration.

temperature, roughness and crystalline properties of the substrate. The critical nucleus radius for PLD is as small as in the range of 1 or two atoms because of its high density of nucleation sites. Therefore the nucleation rate of PLD is high since the nucleation rate is proportional to the nucleation site density and the rate of impingement. As a result, the smoothness of the deposited film is increased due to the high density of nucleation sites.

3.3. TEM specimen preparation

Specimen preparation is critical for materials characterization using TEM. Many literatures ^[153, 154] describe the techniques of TEM specimen preparation. There are mainly two types of TEM specimens, plan view and cross section specimens, which are commonly used in characterization of thin films or their devices. A plan view specimen makes the film perpendicular to the electron beam. Plan view images of a specimen provide information about morphology of individual layer and suitable for performing crystallographic characterization technique such as electron diffraction. Cross section specimens are used to investigate the morphology across the specimen or thin film structure since a cross section specimen allows the interface of thin films parallel to the electron beam giving images of the film structures. Structural and chemical information of individual layer can be obtained. Identification of interfacial reactions in terms of phase transformation and film growth can be made using analytical TEM techniques. In this study, plan view specimens and cross section specimens of the SrFeO₃ films on the substrates of Si/SiO₂, single crystal Al₂O₃ (sapphire) and sintered Al₂O₃ were prepared for TEM examination.

3.3.1. Plan-view TEM specimen preparation

For the preparation of a plan view specimen, a 3-mm disc was cut from the deposited thin film wafer. This piece was ground from the substrate-side to approximately 100 μ m (Fig.

3.3.1.a), followed by dimpling to provide a region with a thickness of about 10µm. Final thinning to perforation was achieved by single sided ion sputtering on the substrate (Fig.3.3.1.b). Specific layers of the multilayered films were accessed by incremental steps of Ar-ion sputtering to remove the upper layers using a Gatan PIPS system (precision ion polish system). Ion sputtering conditions for plan view specimens are chosen depending



a



b

Fig. 3.3.1. Schematic procedure of plan-view TEM specimen preparation.

on the purpose of the sputtering and the material to be sputtered. For thinning, the voltage was set at 4.0 kV for silicon and around 5.0 kV for alumina. The pressure of Ar was set prior to sputtering to have maximum efficiency of sputtering. sputtering angle of Ar incidence ranges form $6-10^{\circ}$. For removing a layer of film, tests with special conditions were made prior to obtain approximate sputter rate as a reference for the film removing.

3.3.2. Cross-section TEM specimen preparation

For cross section specimen preparation, two pieces approximately 5 mm long and 1mm wide were cleaved from the deposited thin film wafer (Fig. 3.3.2.a) and glued together with epoxy adhesive, film side face to face to form a sandwich or a raft-like structure along with pieces of the same size cleaved from a bare silicon wafer which was just over 3 mm thick (Fig. 3.3.2.b). The epoxy was then cured at $T\sim100^{\circ}$ C in air, and the raft was cut to form a disc 3 mm in diameter with a Gatan Ultrasonic Disc Cutter (Model 601).

The disc was mechanically ground using a Gatan specimen grinder with abrasive paper (finished at 600 grit) to a thickness of less than 100 μ m (Fig. 3.3.2.c). The upper and lower surfaces were then dimpled using an EAF Specimen Prep System, Model 2000 and polished with 0.25 micron diamond paste at the final stage to produce a mirror finish and a small hole less than 0.3 mm in the centre (Fig. 3.3.2.d). The edges of the specimen adjacent to the hole were Ar-ion milled using a Gatan Precision Ion Polishing System (PIPS), Model 691 for about 40 minutes at 3-4kV and an incident angle of ~10° to the surface followed by ~20 minutes at ~2 kV. This provided imaging access to the subject film and associated interfaces with the substrate. Cooling with liquid nitrogen is

not needed to prevent specimens form preferential sputtering because of the low incident angle of Ar.



Fig. 3.3.2. Schematic procedure of cross-section TEM specimen preparation

For the films with Al_2O_3 substrate, the extreme hardness of Al_2O_3 increases the difficulty in TEM specimen preparation. Wedge shaped cross section specimens were prepared with modified grinding tools and the interested area at the edge of specimen was finally thinned with Ar ion sputtering. Detail of the method is given in the chapter V.

3.4. Analytical TEM characterization of perovskite thin film systems

Analytical transmission electron microscopy (ATEM) plays an important role in material science owing to its powerful functioning in imaging, elemental detection including electron status and crystal structure determination. The combination of the information from a specimen is sufficient enough to exclusively reveal the nature of an unknown material. The unique advantages of an analytical TEM rely on its high spatial and energy resolution. Ex. the modernized model of an ATEM has sub-micron spatial resolution, less than 0.15 eV energy resolution and smaller than 1 nm beam size, which means three dimension information of all about within a few tens of atomic cluster can be explored. In this study, a Philips CM20 analytical TEM, equipped with an EDS system and a high resolution Gatan UltraScan 1000 CCD camera (2kx2k), was utilized in the microscopy laboratory of the Institute for Chemical Processing and Environmental Technology, National Research Council of Canada. Techniques such as bright field (BF), dark field (DF), high resolution (HR)TEM imaging and ED (electron diffraction) including selected area electron diffraction (SAED) and CBED were used in the characterizations of the crystallographic and interfacial structures of the films.

3.5. Principle and chemical sensing-measurement of conductometric sensing response

One of the important parameter measuring the functionality of a sensor is the resistance ratio R_{air}/R_{gas} or the response ratio $(R_{air}-R_{gas})/R_{air} \times 100\%$, which are influenced by the operating temperature, the concentration of gases and materials used, such as cation and oxygen stoichiometries and morphological structure of the films. Changes in electrical resistance are caused by adsorption of a gas on the surface of semiconductor oxides.

Conductivity and sensing test of the $SrFeO_3/Al_2O_3$ film systems was carried out using the two-wire method^{11, 155} in a controlled environment where the temperature could be varied between 20 and 600°C and composition of the flowing gas changed as required. The schematic illustration of the measurement of conductometric sensing response is shown in Fig.3.5.1. Electrical contacts were achieved by thermally depositing 200nm Au pads directly onto the SrFeO₃ films. Sheet resistances and conductivities of the films were calculated from the resistance measurement and corrected for the geometrical configuration of the Au electrode pads and the thickness of the films, which was assumed to be the same for the thin film systems with the two different substrates. Prior to the determination of the dynamic temperature dependences, the resistances of the films were measured while cooling at a controlled rate of 10°C/min from 500 -100°C in air. For each film, this procedure was repeated at least twice to ensure reproducibility. The sensing responses of the films as a function of the gas composition were measured isothermally at 500°C. This was done by measuring the film resistances as, ex. the O_2/N_2 gas mixtures were varied from air to oxygen-poor ($6\%O_2$) conditions in a stepwise manner, typically waiting 30min before changing to the next composition. The gas was then changed in the reverse order from oxygen-poor to air in order to verify reversibility. More detailed experimental procedures and conditions can be found elsewhere. [11, 155-156]



Fig. 3.5.1. Schematic illustration of measurement of conductometric sensing response.

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Chapter 4

Thermal Stability of SrFeO₃/SiO₂/Si Thin Film System: TEM Investigation of Interfacial Reactions between SrFeO₃ Thin Films and Silicon Substrates

4.1. Introduction

 $SrFeO_{2.5+x}$ materials can be used as thin film gas sensors ^[1, 7-11, 54, 157-159] since the reversible uptake of oxygen at elevated temperatures can readily occur, and this is accompanied by significant changes in electrical conductivity which can be monitored as the sensor transduction signal.

The electrical and gas sensing properties of films of these material types are strongly dependent on the cation and oxygen stoichiometries ^[9] and also on film morphology.^[160-163] However, both the structure and the morphology of the films are dependent upon deposition temperature, and studies have shown that films deposited at different temperatures have varying degrees of crystallinity and preferential orientation.^[164, 165] Films which exhibit texture or no crystallinity show limited sensor functionality and cannot easily and reversibly transform from the brownmillerite to the cubic perovskite structures. Thus, a full understanding of the effects of deposition conditions, especially the roles of deposition temperature and post-deposition thermal treatments, on the film structure is crucial for optimizing the gas sensor response characteristics.

In addition to the sensitivity and rapid response of the sensors, thermal stability of the thin film must also be considered to ensure longer term signal reproducibility because

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perovskite based gas sensors are operated at elevated temperature in order to provide a rapid sensor response. The perovskite materials may be unstable under certain thermochemical conditions,^[18] and at the elevated operating temperatures of ceramic-based gas sensors, the films may react with the underlying substrate.^[19-25] This is especially important for MEMS based sensors using silicon-based sensor platform structures,^[166] since silicon is known to react with many materials at elevated temperatures (T>300 °C).^[21-25, 167-168] Therefore a comprehensive understanding of the inter-relationships between the thin film sensor material and the underlying substrate is crucial in determining sensor stability and design, especially for devices which will be operated at elevated temperatures (>300 °C).

In this chapter, the study of the thermal stability of thin film system $SrFeO_{2.5+x}/SiO_2/Si$ is discussed. A silicon substrate with a SiO_2 buffer layer in contact with the $SrFeO_3$ thin film is considered in order to see the role that SiO_2 plays in the thermal stability of the system. Thin films of $SrFeO_{2.5+x}$ where x>0.4 (hereafter designated as $SrFeO_3$) have been grown onto single crystal silicon substrates with a SiO_2 buffer layer by the pulsed laser deposition (PLD) technique. The films have been prepared under different growth conditions and subjected to post-deposition thermal treatments. The structure of the film and interface regions was comprehensively investigated using analytical transmission electron microscopy including high resolution imaging, electron diffraction and energy dispersive spectrometry.

4.2. Experimental Procedure

4.2.1.. Material preparation

(a) Target material for SrFeO₃ deposition

Powdered SrFeO₃ was synthesized by conventional ceramic preparation techniques. Stoichiometric amounts of SrCO₃ and Fe₂O₃ precursor powders (Alfa-Aesar >99.99% purity on a metal basis) were mixed and ground, and then heat treated at 1100°C under oxygen in a tube furnace for 36 hours. The sintered product was then ground and characterized by x-ray diffraction (XRD), (Bruker Axis D8 diffractometer, monochromatic Cu-K_{α} radiation, scan range 5° $\leq 2\theta \leq 100^{\circ}$; step size 0.03°; dwell time 2s), to ensure that a single-phase product was obtained. The SrFeO₃ powder (2g) was then pelletized in a mold in a hydraulic press at 2T and re-sintered at 1150°C in oxygen to yield a dense cylindrical pellet with dimension 12mm(dia) x 5mm. Further XRD analysis confirmed the SrFeO₃ pellet to be single phase.

(b) The substrate SiO₂/Si

A Si (111) wafer with a thermally grown $1\mu m$ SiO₂ buffer layer was chosen as the thin film substrate. The wafer was cleaved to 10x10 mm pieces. A piece of substrate was cleaned with water and rinsed with acetone and alcohol before being attached to specimen holder for film deposition.

4.2.2. Pulsed laser deposition (PLD)

The SrFeO₃ pellet was then used as the target for the deposition of SrFeO₃ thin films by the pulsed laser deposition (PLD) technique. The excimer laser used was a Lambda Physik LPX305i, operating with Kr/F (λ =248nm); other system details are reported elsewhere.^[11] During deposition, the temperature of the Si/SiO₂ substrate was maintained at either room temperature (RT~22°C) or 700°C. All films were deposited for 4 minutes at a laser pulse rate of 8Hz, pulse duration of 25ns, fluence of ~1.5 J.cm⁻² and under a background oxygen pressure of 100 mTorr. The average deposition rate was about 10 -20 nm per minute depending on deposition temperature, producing films of approximately 40 – 80 nm thickness.

4.2.3. Post deposition thermal annealing

Post thermal annealing for samples was carried out in a tube furnace with controlled gas flow. Annealing temperatures were chosen based on the purpose of the study for each thin film system. Heating of the samples was performed in air. The overall deposition and thermal heat treatment conditions for the samples studied in this chapter are listed in table 4.2.3.

		Annealing		
Thin film system	Deposition at (-°C)-for(- min.)	Heating at (- °C) for (- hr.), and at rate °C/min	Cooling, °C/min	
SrFeO ₃ /SiO ₂ /Si	RT - 04			
SrFeO ₃ /SiO ₂ /Si	450 - 04			
SrFeO ₃ /SiO ₂ /Si	700 - 04			
SrFeO ₃ /SiO ₂ /Si	700 - 04	700 - 01, 10	20	
SrFeO ₃ /SiO ₂ /Si	700 - 04	700 - 02, 10	20	
SrFeO ₃ /SiO ₂ /Si	700 - 04	700 - 03, 10	20	

	Table 4.2.3. List of s	pecimens with d	eposition and	thermal	treatment conditions.
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4.2.4. TEM specimen preparation

Cross section and plan view specimens of the SrFeO₃ films on the SiO₂ /Si substrates were prepared for TEM examination.^[169, 170] Detailed procedures of cross-section and plan view TEM specimen preparation are described in Chapter 3. The specific layers of the multilayered films were accessed by incremental steps of Ar-ion sputtering to remove the upper layers using a Gatan PIPS system. The sputter rate depends on many factors such as the gun voltage, the pressure of the Ar, the material, the nature of preferential sputtering of the elements in the material and the thickness of the film to be sputtered. Sputtering on samples similar to the material to be studied is necessary. This data can then be used as a reference for the actual TEM specimen sputtering. Note that it is not necessarily the case that the lower the sputter energy (the ion gun voltage), the smoother the sputtered area, and the smaller the impinging angle of the Ar-ion, the larger the thinned area will be. There is a threshold of energy for an atom in each material to be removed by sputtering. A combination of impinging angle and the ion power should be considered for a given material. This is because binding energy is different from material to material and sputtering is a complex procedure so that material removal and deposition are occurring at the same time.

4.2.5. Thin film structure characterization using analytical TEM

Characterization and imaging by TEM was done using a Philips CM20 TEM system equipped with an energy dispersive x-ray spectrometer: INCA Energy TEM 200 and a Gatan UltraScan 1000 CCD camera (located in NRC, ICPET TEM lab). An accelerating voltage of 200kV was selected for TEM imaging and a beam diameter smaller than 10nm was used for EDS chemical composition analysis. Bright field (BF), dark field (DF), high resolution (HR) TEM imaging and electron diffraction (ED) techniques were used in combination to investigate the crystallographic and interfacial structures of the films.

4.3. Results and Discussion

4.3.1. Structures of SrFeO₃/SiO₂/Si thin films deposited at room temperature

(a) TEM characterization of the thin film system

The BF TEM images obtained from a cross section specimen of the $SrFeO_3/SiO_2/Si$ thin film system deposited at ambient temperature are shown in Fig. 4.3.1. The $SrFeO_3$ film was measured to be 46nm in thickness and the adjacent buffer layer of SiO_2 was 1.14 µm in thickness (Fig. 4.3.1a). High resolution TEM (HRTEM) images (Fig. 4.3.1b) show that



(a)

Fig. 4.3.1.(a) TEM micrographs from a cross section specimen of the SrFeO₃ thin film deposited onto the SiO₂/Si substrate at room temperature for 4 minutes. A complete view of the cross section of the thin films system is shown. (to be continued)



Fig. 4.3.1 (continued) (b) HRTEM image of the thin film of $SrFeO_3$ and its adjacent SiO_2 layer from a cross section specimen of the $SrFeO_3$ thin film deposited onto the SiO_2/Si substrate at room temperature for 4 minutes. The $SrFeO_3$ thin film consists of a layer of crystalline nano-sized $SrFeO_3$ grains and a layer of featureless domains adjacent to the amorphous SiO_2 layer (to be continued).

the SrFeO₃ film is constituted by two regions. One is a layer of nano-sized grains, about 5 nm in diameter, it can be seen that the fringe features in the film indicated by an arrow and labelled as crystalline SrFeO₃ in Fig. 4.3.1b is the characteristic of a crystalline structure. The other, beneath the nano-grains, is a layer of featureless domains interfacing with the amorphous SiO₂ buffer layer. An amorphous/single crystal structure characterizing the interface between the silica layer (SiO₂) and the silicon (111) substrate is shown in Fig. 4.3.1c. Energy dispersive x-ray analysis (EDS) (Fig. 4.3.1d) confirms that the SrFeO₃ film had an elemental composition corresponding to that of the target used in the PLD step. This was done by taking the target material (confirmed to be



(c)



Fig. 4.3.1(continued). (c) HRTEM image showing the interface of SiO_2 /Si of a cross section specimen of the SrFeO₃ thin film as shown in (a), and (d) EDS spectra showing the chemical composition of the SrFeO₃ layer.

SrFeO₃ by x-ray diffraction during target preparation) as the standard SrFeO₃ material for EDS analysis. EDS analysis on both target and thin film specimens were achieved under the same TEM conditions: 200 kV, nanoprobe size <10nm and 1 minute living time with less than 6% dead time. A quantitative result was obtained by comparing the relative ratio of the intensity (peak heights-background) of the Sr, Fe and O elements in the EDS spectra of these two materials. No chemical inter-diffusion of elements was found across the SrFeO₃ / SiO₂ interface. For the SrFeO₃ film which is adjacent to the SiO₂ layer, there exists a 15 nm layer which shows featureless domains, and is likely to be amorphous (Fig 1b). This implies that the amorphous SiO₂ layer provided a surface unfavorable to the required conditions to induce nucleation of SrFeO₃. Consequently, an amorphous SrFeO₃ region initially forms on the SiO₂ as a transition zone prior to the nucleation of crystalline SrFeO₃.

(b) Differentiation of crystallographic characterization between HRTEM and x-ray on thin film

It should be noted that in film characterization, x-ray diffraction is an often used method to determine or identify the phase(s) or other crystallographic features of the deposited film(s). However, uncertainty for x-ray in thin film characterization could occur, in other words, in some cases x-ray diffraction cannot provide reliable information for determining the crystallography of the phases in the thin films. This is because, firstly, x-ray diffraction usually produces very low relative reflection intensities of the thin film to the substrate owing to very thin film thickness. This is one of the obstacles to identify the film structure. Secondly, the likelihood of internal stress in the films can shift the

position of the diffraction peak away from the Bragg position of the corresponding phase free of internal stress resulting in difficulty in phase identification. Finally, and the most importantly, is the grain size effect which is a direct factor affecting the width of the reflection peak, *i.e.* smaller grian sizes produce broader reflection peaks. This is because except for the internal crystal defects such as twin boundaries and dislocations located in the center of the grains, the surface of the grains is the main concern in considering the effect of crystal defects on broadening of the XRD peaks. The surface defects of a crystalline grain usually penetrate several layers of atoms deep into the grain. In the surface defect region, dense point defects and line defects exist, such as vacancies, interstitial atoms and dislocations, suggesting that the atomic arrangement does not reflect the periodic nature of the bulk crystal structure. For the nano-scaled crystalline grains, this effect is significant since the relative amount of the defect volume (e.g., surface region) in a grain is large. Also surface energy cause severe crystal distortion to a nanoscalled grain or particle. Defects in a crystal and distortion of crystal structure weaken the constructively interfered x-ray beam and provide information reflecting diffraction from crystal planes with a range of interplanar spacings. Therefore, widened and weakened reflection peaks occur in the x-ray diffraction profile of a nanostructured thin film or nanoparticles which gives reduced information about the crystallographic nature. As a result, nanostructured thin films or nanoparticles can be then considered to be amorphous because there is no diffraction peak that can be recognized. Shown in Fig. 4.3.1e is the x-ray diffraction of the SrFeO₃/SiO₂/Si (111) thin film system grown at room temperature for 4 minutes. The intense peak at $2\Theta = 28.4^{\circ}$ represents the reflection from the Si (111) substrate with highest intensity (partial scale of the profile is shown).

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On the other hand, the information about the film shown on the background profile is extremely limited. The only information about the SrFeO₃ film is represented by the broad peak at about $2\Theta = 20^{\circ}$. Therefore, the x-ray diffraction pattern shown in Fig. 4.3.1e cannot confirm that a crystalline SrFeO₃ phase exists in the film. Glancing angle xray diffraction decreases the difference in intensities of peaks between film and substrate, or even gets rid of the information from the substrate, but it does not generally improve the proviision of information about nano-structured materials. However, the film is identified by the cross-section lattice image of the film through HRTEM imaging (Fig.4.3.1b) to be nano-crystalline at the top layer. In many similar cases of thin film xray diffraction, an amorphous film is wrongly confirmed to be crystalline or it is the other way round. HRTEM imaging has shown its advantage over the x-ray diffraction in thin film characterization by providing a direct view of lattice images, which is exclusive in determining crystalline structure.



Fig. 4.3.1e. x-ray diffraction of the thin film system $SrFeO_3/SiO_2/Si$ deposited at room temperature for 4 min. Crystalline $SrFeO_3$ layer cannot be recognized.

4.3.2. Structures of SrFeO₃/SiO₂/Si thin films deposited at 450°C

An as-deposited thin film of SrFeO₃/SiO₂/Si grown at 450°C for 4 min was investigated. Shown in Fig. 4.3.2 is the BF TEM cross section micrograph of this system. Note that the image (Fig. 4.3.2) shows a surface to surface contact of the films with a light colored layer (epoxy), this is because two pieces of sample material were glued face-to-face (films contact each other) during the cross section sample preparation, and epoxy was used to adhere the sample pieces. The image shows that the total thickness of the SrFeO₃ film is 85nm with principal features in the SrFeO₃ film that distinguish two types of layer on the SiO₂ buffer layer of the substrate: an upper region of about 15-20 nm containing a layer of crystalline grains denoted as Sr-Fe-O and a lower layer of about 60-65nm amorphous underneath the crystalline layer denoted as Sr-Fe-O-Si because Si is detected



Fig.4.3.2. BF TEM micrographs taken from the thin film system $SrFeO_3/SiO_2/Si$ deposited at 450°C for 4 minutes.

by EDS. Compared with the SrFeO₃/SiO₂/Si system deposited at room temperature, a

much thicker SrFeO₃ film is observed in the film deposited at 450°C, indicating that significantly faster growth of the amorphous phase occurred under these deposition conditions. The two-layer structure in the film is similar to that of the film deposited at room temperature but with different relative thicknesses between the crystalline part and the amorphous part. This feature remained unchanged until deposition at higher temperature. Detailed characterization of the thin film structure will be discussed in the next section.

4.3.3. Structures of SrFeO₃/SiO₂/Si thin films deposited at 700°C and post-

deposition thermal treatment

(a) Structures of SrFeO₃/SiO₂/Si thin films deposited at 700 °C for 4 minutes

An as-deposited thin film of $SrFeO_3/SiO_2/Si$ grown at 700°C for 4 min was investigated. Shown in Fig. 4.3.3 (a-c) are BF TEM cross section micrographs of this system. The image (Fig. 4.3.3a, b) shows a surface to surface contact of the films with a light colored layer (sample preparation adhesive) in between. The total thickness of the $SrFeO_3$ film is 70nm with principal features in the $SrFeO_3$ film that distinguish two types of layer on the SiO₂ buffer layer of the substrate: an upper region of about 15nm and a lower layer of about 55nm adjacent to the SiO₂.

Overall, the SrFeO₃ film is much thicker compared with the SrFeO₃/SiO₂/Si system deposited at room temperature, as shown in Figure 4.3.2a, but is thinner than that in the system deposited at 450° C, i.e. 80nm. The upper layer of the film contains a continuous layer of crystalline grains denoted as Sr-Fe-O, embedded in the layer underneath which is

amorphous and denoted as Sr-Fe-O-Si. The grains are aligned on the surface to form a layer about 15 nm thick. The layer of amorphous phase labeled as Sr-Fe-O-Si in Fig. 4.3.3b, which is a cross section image of the film system with higher magnification, shows a continuous layer of grains on the surface of the film. The two-layer structure in the film is similar to that of the film deposited at 450°C. In addition, the cross section



(a)





Fig.4.3.3. BF TEM micrographs taken from the thin film system SrFeO₃ /SiO₂/Si deposited at 700°C for 4 minutes. (a) The cross section of the film/ substrate structure containing top grains labeled as Sr-Fe-O. (b) Image of (a) with higher magnification and (c) the plan view of the crystalline SrFeO₃ thin film. and plan view images of the crystalline grains presented in Fig. 4.3.3c show that the dimension of the grains is predominantly around 15 nm. The SiO_2/Si interface structure remained the same as in the case of the film deposited at room temperature.

The two-layer structures (crystalline and amorphous) of the thin film appearing in the thin film systems deposited at RT, 450 and 700C° indicate that the amorphous phase grows more dominantly with an increase in temperature (15-80 nm amorphous layer observed in a temperature range of RT-450C°) but then less so at a higher temperature (70 nm observed at $700C^{\circ}$). The phenomenon of the amorphous growth occurring in the high temperature deposited film implies that the overall thermodynamic and kinetic situation of the amorphous material must favour it over that of the crystalline structure. From the thermodynamic point of view, the entropy of creating the amorphous phase is greater than for the crystalline structure, since dG/dT = -S (at constant pressure, i.e. dp = 0), where G is Gibbs free energy, T is temperature and S is entropy. This means the gradient of the free energy G vs. temperature T is equal to the negative value of the entropy of the system, suggesting that increasing the temperature will result in decreasing the system energy faster for the amorphous over the crystalline form, since the amorphous state of a material possess higher entropy than its crystalline state. Even though the crystalline system is the thermally stable phase rather than the amorphous, amorphous growth is still possible because it reduces the system energy more rapidly compared with the growth of its crystalline phase. Formation of an amorphous phase other than any stable crystalline phases in a given thin film system can be also due to kinetic constraints on crystalline phase nucleation. ^[78] One of the possible kinetic

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constraints suggested is "kinetic interfacial barrier", i.e., the absence of a low energy or coherent interface between the crystalline compound and the substrate materials of the thin film system. ^[80] The kinetic obstacles to prevent the crystalline phase to form, in turn, include the grain boundaries which increase the free energy of the system. Atoms need sufficient activation energy to overcome the energy barrier in order to rearrange the atoms to the positions in the long range crystal lattice. Changing from the amorphous growth to the crystalline phase formation should occur when the temperature is high enough. Another factor affecting the amorphous growth, in the case under discussion, is the participation of the amorphous SiO₂, which provides a source of Si into the thin film, as a result of diffusing and/or reactions at the film/SiO₂ interface. This situation could favour the growth of the amorphous phase of the film. However, the thinner amorphous layer (~70nm) appearing in the thin film deposited at 700C^o implies that the growth of the amorphous phase has stopped and further changes could happen upon subsequent thermal treatments.

EDS analysis of the film on a cross section sample showed that the elemental compositions were different from those found in the films deposited at room temperature. Although the elemental composition of the deposited film (nanocrystalline) is identical to that of the phase SrFeO₃, a slightly larger relative amount of iron is present in the crystalline grains shown in Fig. 4.3.4a, as compared with the spectra of the crystalline SrFeO₃ phase shown in Fig. 4.3.1d. The slight variation from the stoichiometry of SrFeO₃ implies that a structural defect or even phase transformation could occur. Significant compositional differences between the crystalline and the amorphous phases in the film

deposited at 700°C can be seen from the spectra shown in Fig. 4.3.4a and b, i.e., in the amorphous phase of the film, a smaller relative amount of iron and significant amount of Si are present, unlike the case of the room temperature deposited film where the composition in the nanocrystalline and amorphous regions are identical. Note that since



Fig. 4.3.4. EDS spectra of the thin film system $SrFeO_3 / SiO_2 / Si$ deposited at 700°C for 4 minutes, (a) from the crystal grains in the film, (b) from the amorphous phase of the film and (c) from the SiO₂.

the Si (K_{α}) peak (at 1.739keV) and the Sr(L_{α}) peak (at 1.806keV) overlap in the EDS spectra, the existence of silicon in the crystallites cannot be confirmed by distinguishing these two peaks in the EDS spectra, particularly when the relative amount of silicon is small. However, by comparing these spectra with those for SrFeO₃, the existence of Si can be confirmed by

calculating the ratio of the peak height of Sr(L) to Sr(K) or Sr(L) to Fe(K) in each spectrum, respectively, and taking that for SrFeO3 as a standard for calibration. Note, the peak height representing an element is used, instead of the integrated intensity of the element. This is because $SrFeO_3$ is used as the standard material, comparing the peak height ratio of a material relative to that of the standard material is simple and the result is reliable, especially in the case of TEM for EDS qualitative analysis, where the instrument operational conditions are identical and the analyzed areas in the specimens (the sample material and the standard materials) are selected to be identical in thickness. The specimens are so thin that the effects of x-ray absorption and fluorescence can be neglected so that the generated x-ray intensity and the x-ray leaving the specimens are identical. Therefore, the difference between the height ratio measurement and the intensity measurement is negligible. As a result, the amorphous part of the film is determined to contain additional silicon (Fig. 4.3.4b). EDS also confirmed that in the SiO_2 region close to the SrFeO₃/SiO₂ interface, there was no Fe or Sr present (Fig. 4.3.4c). Interfacial structures and composition analysis indicate that deposition at the higher temperature results in increased growth of the amorphous phase through reaction between SiO₂ and the crystalline grains in the film and further diffusion of Si in the amorphous layer. Reaction of deposited film material with SiO_2 can be considered as a

result of interdiffusion of oxygen toward the substrate and Si outward into the film.

Crystallographic characteristics of the film were also determined. Shown in Fig. 4.3.5a is a cross section image of an individual grain which shows a single crystallite attached to two or three smaller grains as indicated by an arrow. Since the outermost part of the film represented by the larger crystallite appears to be preferentially orientated and boundaries occur between the larger crystallite and the attached smaller grains, the possibility of a multi-phase region was taken into account in phase identification. In order to identify these crystalline phases, a plan view specimen was prepared to remove the outermost crystallites by argon ion sputtering, leaving the small grains underneath remaining as shown in the upper left area of Fig. 4.3.5b. A selected area (SA) electron diffraction pattern (EDP) (Fig.4.3.6a) was then obtained from this area. The EDP shown in



Fig. 4.3.5. (a) A cross section image of an individual grain from the $SrFeO_3 / SiO_2 / Si$ thin film system deposited at 700°C for 4 minutes showing that a single crystallite is attached to two or three small grains. (b) A TEM plan view image of the film showing the crystalline grains, where the top layer crystallites (near the top-left area) are removed.

Fig.4.3.6b was obtained from the outermost larger grains of the non-surface sputtered film as shown in Fig. 4.3.3c. For comparison, an EDP of polycrystalline SrFeO₃ is also presented in Fig.4.3.6c. It is apparent that the EDPs shown in Fig.4.3.6a and b are different from those of SrFeO₃. The small difference in chemical composition between the grains in the as-deposited film and the crystalline SrFeO₃, as shown in Fig. 4.3.4a and Fig.4.3.1d respectively, is not a strong driver to produce a critical impact on the crystal structure of the film. So, the slight difference in chemical composition of the grains in the as-deposited film from that of SrFeO₃ cannot be be argued to support that this difference has caused phase transformation of grains (SrFeO₃). Also, the compound SrFeO₃ is thermally stable at the deposition temperature. Therefore, it is reasonable to assume that the crystal structure of these crystalline grains still remains the same as that for SrFeO₃. The slight difference in composition could only introduce crystal defects to the SrFeO₃ structure. The differences in the EDPs imply that the crystallites possess preferential orientations.

The pattern shown in Fig, 4.3.6a consists of a set of diffraction rings including the low angle diffuse ring close to the center BF spot. The diffuse ring occurring together with ring patterns indicates that a mixture of amorphous and crystalline phases exists. The amorphous phase, in this case, is likely to be the Sr-Fe-O–Si compound with short-range ordered domains (Fig. 4.3.6d). A sharper diffraction ring overlaps the diffuse ring shown in Fig.4.3.6a suggesting that reflections from crystals represent those crystalline planes with a d-spacing identical to the average atomic spacing of the short-range ordered domains in the amorphous phase.



Fig.4.3. 6. For the $SrFeO_3 / SiO_2 / Si$ thin film system deposited at 700°C for 4 minutes, (a) an SAD pattern from the top-left area near the edge shown in Fig.4.3. 5b indexed as ZA=[112]. (b) An SAD pattern from the outmost larger grains of the non-surface sputtered film as shown in Fig.4.3.2c indexed as ZA=[111]. (c) An ED pattern from SrFeO₃. (d) An image of the amorphous phase Sr-Fe-O–Si with atomic short-range ordered domains.

The interface between the crystallites and the amorphous phase becomes the location of a growth front of the amorphous phase as it consumes the crystallites in the film. The evidence is that the amorphous layer contained in the film at this deposition temperature (700C°) is thicker and the crystalline layer of the film is thinner compared with that in the RT deposited system. Therefore, it can be inferred that the growth mechanism depends on the initial formation of the amorphous layer of the film, and is followed by its growth while the species of thin film material are still being deposited. The deposited species nucleate on the amorphous layer and then react with the amorphous phase resulting in amorphous growth. In the mean time the nuclei of the deposited material grow and the species of the film material continue to nucleate and grow. Consequently, the small grains attached to the outmost crystallites can be considered to be either the primary nuclei on the amorphous phase or the remnants of the crystalline phase following amorphous grow with a new preferred orientation.

Assuming that the crystalline grains possess the pseudo cubic structure of $SrFeO_3$, then those crystallites adjacent to the amorphous phase (Sr-Fe-O-Si) have a preferential orientation of [112] perpendicular to the film surface as indicated in Figure 4.3.6a. The diffraction patterns from the crystallites at the top surface of the film give d-spacings closest matching the d₁₁₀ and d₂₁₁ of the (110) and (211) planes of the phase SrFeO₃, (d₁₁₀ = 0.2635nm, d₂₁₁ = 0.1516nm for SrFeO₃ indicated in the Powder Diffraction File, PDF, PDF# 34-0641). The difference of the measured d-spacings for the crystallites is less than 4% from the d-spacings shown in the SrFeO₃ PDF file. As a result, a preferential orientation of [111] is determined to be present in the outermost grains, since only the diffraction pattern with ZA = [111] allows both the (110) and (211) reflections to occur simultaneously. Although the two sets of SA EDPs share some similarities, differences are present between the patterns as shown in Fig. 4.3.6a and b. For example, the d-spacings calculated for the diffraction rings with similar intensities in the two sets of patterns, i.e., the diffraction rings indexed as (220) in Fig. 4.3.6a and (211) in Fig. 4.3.6b are not identical $(d_{220})_{ZA=[112]} = 0.9 (d_{211})_{ZA=[111]}$). Hence, different preferential orientations were considered to be present for the grains as discussed above, and they are indexed as ZA= [112] and ZA= [111] for crystallites adjacent to the amorphous phase (Sr-Fe-O-Si) and outermost crystal grains, respectively.

It should be noted that since the film was deposited on a single crystalline Si (111) wafer with a SiO₂ buffer layer, the preferential orientation of the crystalline grains are determined by initially obtaining an electron diffraction pattern from the substrate Si area with zone axis ZA = [111], which is perpendicular to the surface. The electron diffraction image was then taken from the region of interest by translating the specimen using the TEM specimen holder. Considering that an amorphous buffer layer of SiO₂ exists between the deposited film and the single crystal Si substrate, this acted as a barrier and prevented the nucleation and growth of the crystalline grains of the deposited film from the influence of the crystalline Si substrate. Therefore, it is more meaningful to take the orientation of the surface rather than that of the Si as the reference for defining the preferential orientation of the crystal grains in the film. However, the orientation of the area chosen for electron diffraction could be tilted from the perpendicular to the Si [111] direction, and this is attributed to the localized tilt of the film due to a combination of film deformation and the setting precision of the specimen holder.

(b) Structures of SrFeO₃/SiO₂/Si thin film system deposited at 700 °C for 4min plus annealing at 700 °C for 1 hour

To investigate whether phase transformation or phase separation could occur in the films during heating at elevated temperature, TEM examination was performed on the thin film system SrFeO₃/SiO₂/Si grown at 700°C with a further one hour of thermal annealing at $T=700^{\circ}$ C in air following the deposition. TEM images and EDS spectra for this film are shown in Fig. 4.3.7. Annealing produces some significant structural modifications compared to as-deposited films. The thickness of the SrFeO₃ film was reduced to 52nm, which includes about 10 nm of a crystalline phase (grains) on the top surface and 42 nm of an amorphous phase underneath (Fig.4.3.7 a and b). One of the possible causes of reduced film thickness is an increase in film density during crystal growth. Also, a continuous crystalline layer of Sr-Fe-O in the film is observed in Fig.4.3.7b, consisting of disk-like grains with lattice-scaled lamellar features parallel to the surface (see HRTEM image in Fig.4.3.7c). The crystallites are well formed unlike the grains shown in Fig.4.3.5a, and are embedded in the amorphous Sr-Fe-O-Si phase. The interface between the film and the SiO₂ of the substrate is no longer as flat as it was before annealing, implying that an interfacial reaction occurred during deposition and/or annealing.

Analysis by EDS showed the elements in each phase to be the same as those present in the sample prior to annealing. However, the relative amount of (Sr, Fe and O) in the







Fig.4.3.7. TEM cross-section micrographs of the $SrFeO_3$ /SiO₂/Si system deposited at 700°C with a further one hour thermal annealing at T=700°C. (a) showing the film/ substrate structure. The film contains crystallites on the top labeled as Sr-Fe-O, despite of presence of silicon, and an amorphous phase labeled as Sr-Fe-O-Si. (b) An image with higher magnification from the area of the film. (to be continued)







Fig.4.3.7. (continued) TEM cross-section micrographs of the SrFeO₃ /SiO₂/Si system deposited at 700°C with a further one hour thermal annealing at T=700°C. (c) A HRTEM image of a single crystallite in Sr-Fe-O. (d) and (e) EDS spectra from the Sr-Fe-O and Sr-Fe-O-Si layer respectively.

crystalline layer is significantly different (Fig.4.3.7d) with the relative amount of Fe is reduced, or increased. Also, for the amorphous phase, either the relative amount of Fe is reduced, or the amount of strontium is increased (Fig.4.3.7e). This is in addition to the existence of a significant amount of Si which has been shown to be present in the amorphous phase in the sample prior to annealing. By analyzing the spectra shown in Fig.4.3.7d and comparing with the spectra for SrFeO₃, it is reasonable to assume that silicon is present in the arrest layer and it is a phase with composition richer in Fe relative to Sr.

Shown in Fig.4.3.8a is an EDP obtained from the crystallites present in the outermost layer of the film after annealing at 700°C for 1 hour. This diffraction pattern differs from any obtained with the previously discussed samples. Combining the information of the electron diffraction and the EDX analysis, the crystallites are considered to evolve from the grains shown in Fig.4.3.5a as a result of annealing. It is proposed that this phase possess an A-site cation-deficient type of perovskite (A_xBO_3) structure where A is the larger element Sr, and B, the smaller element Fe in this case. This implies that elemental redistribution has occurred at the interface with the Sr-rich amorphous phase Sr-Fe-O-Si. Since the BO₃ array in the perovskite structure forms a stable network, the large A cations at twelve-coordinated sites can be vacant either partially or completely.¹⁷¹ Perovskite oxides which are A-site deficient are known to form when B=Ti, Nb, Ta *etc.*^[172-176] Having examined the series of d-spacings converted from the diffraction pattern shown in Fig.4.3.8a, the phase which gives closest match is SrFe₁₂O₁₉ (PDF#46-0335). However, the *d*-spacing indicated by the diffraction pattern cannot uniquely

identify the phase as a known Sr-Fe-O compound at this stage, due to incomplete diffraction data because of preferred orientation effects. Therefore, a conclusive identification cannot be found by solely employing a *d*-spacing match with a known compound. A Fourier transform (analogy to diffraction, not shown here) from a single crystal as shown in Fig.4.3.6c yielded a lattice periodicity of 1.1545 nm in the direction perpendicular to the lamella layers of the crystallite structure implying a lattice parameter which could be equal to $n \times 1.1545$ nm (where n is an integer).

Definitive crystal structure identification of the outermost crystallites was achieved by combining HRTEM image analysis with electron diffraction obtained from the film system with longer-term annealing, at $T = 700^{\circ}$ C for 3 hours in this case. Crystal growth during this thermal treatment results in the evolution of preferential orientation as seen in Fig.4.3.8b showing stronger texturing compared with that present in Fig.4.3.8a. Although the preferential orientation limits identification of the structure by electron diffraction due to an incomplete series of diffraction rings, it does facilitate crystallographic analysis using HR imaging. Thus, the crystal structure of the crystallites was revealed by HRTEM images obtained along its lattice direction. The c direction has been identified in the cross section as being perpendicular to the surface. The a and b lattice parameters of the crystallites were subsequently determined by obtaining a DF TEM image (Fig.4.3.8c) from the (110) diffraction beam indicated in Fig.4.3.8b to confirm the corresponding relationship between the diffraction and the crystallites on the top surface of the film. HRTEM images from the crystallites were then obtained as shown in Fig.4.3.8d along with its processed image aided by fast Fourier-transform (FFT) shown in Fig.4.3.8e





Fig.4.3.8. (a) and (b) ED patterns of the crystallites in the film deposited at 700°C with a 1 hour and 3 hours annealing at T=700°C respectively. Differences are due to development of preferential orientation of the crystallites. (c) A DF image from the diffraction beam indicated by the index 110 in (b). (to be continued).



Fig.4.3.8. (continued) (d) A HRTEM image of an individual crystallite from the plan view specimen shown in Fig.4.3.7(c). (e) The filtered image aided by FFT of the crystallite shown in (d), which represents the lattice projection along c exhibiting a hexagon with a = 0.5876 nm. (f) A HRTEM image of a individual crystallite and its FFT filtered image (g) which represents the projection of the lattice along the direction parallel to the crystal plane shown in (e) with a periodicity of c=2.305 nm.

which represents the lattice projection along c exhibiting a hexagonal lattice with a = 0.5876 nm. A HRTEM image and its FFT processed image shown in Fig.4.3.8f and g represent the projection of the lattice along the direction parallel to the crystal plane shown in Fig.4.3.8e exhibiting a periodicity of the lattice, c=2.305 nm, which is approximately equal to twice 1.145 nm described above as a possible lattice periodicity, suggesting that a sub-lattice structure exists and that the lattice parameter of the crystallites is c = 2.305 nm. The result is a match to the phase $SrFe_{12}O_{19}$ which is hexagonal with parameters a=0.5887 nm and c=2.304nm. Therefore, this phase is isostructural with $SrFe_{12}O_{19}$. Considering that silicon is present in this phase, the overall structure is suggested as a type of intergrowth of perovskite ABO₃ and BO₃ with oxygen vacancies and Si partially replacing Fe, with a formula denoted as $Sr(Fe,Si)_{12}O_{19}$.

(c) The mechanism of the evolution of the phase transformations in the $SrFeO_3/SiO_2/Si$ system

The mechanism of the evolution of the phase transformations in the SrFeO₃/SiO₂/Si system has been developed from data presented by the images shown in Fig. 4.3.9. Fig. 4.3.9a is an image indicating that the lamellar lattice structure of the crystallites extends through a transition zone into the amorphous phase surrounding it. Crystalline growth occurs gradually through a process of atomic rearrangement in the transition zone. Another type of atomic rearrangement has also occurred in the phase transformation, as indicated by an arrow in Figure 4.3.9b. This transformation appears to be due to the movement of atoms through the amorphous matrix phase towards the growing crystalline phase by way of filling the atomic lattice steps at the interface. Thus, the new phase

grows by consuming the amorphous matrix phase.



Fig.4.3.9. HRTEM images from the $SrFeO_3 /SiO_2 / Si$ system deposited at 700°C for 4 minutes and annealed for 1 hour showing the growth of a crystallite into the amorphous surroundings by means of atomic rearrangement through the transition zone (a), and atoms fill from the amorphous phase to the steps of a crystal plane indicated by the arrow (b).

(d) Structures of SrFeO₃/SiO₂/Si thin films deposited at 700°C for 4 minutes plus annealing at 700°C for 3 hours

With increasing annealing time, the phase transformation and phase separation further develop in the films. Fig.4.3.10a shows a cross section image of the film system deposited at 700°C for 4 minutes and then annealed for 3 hours. The crystallites no longer retain layer-like continuity at the outermost surface of the film and the number of the crystallites is reduced. This implies that crystal growth has occurred, with crystallites predominantly displaying two orientations; one parallel and one almost perpendicular to the surface of the film. Additionally, a row of nano-sized grains appear in the SiO₂ layer near the Sr-Fe-O-Si / SiO₂ interface shown in Fig.4.3.10a, the structure of which is not identified due to its extremely small size. Evidence for further phase separation is found, as shown in Fig.4.3.10b where small crystal grains have precipitated from the amorphous matrix adjacent to the lamellar structure of the phase Sr(Fe,Si)₁₂O₁₉. A HRTEM image with lattice fringes shown in the inset of Fig.4.3.10b indicates that the precipitates are crystalline and \sim 3nm in diameter. The precipitates are shown to have a strontium oxide (SrO_X) composition by EDS analysis as shown in Fig.4.3.10c. The occurrence of these crystalline grains is an indication of initiation of crystallization in the amorphous phase

4.3.4. Summary of the evolution of interfacial reactions

(a) Model for interfacial reactions of the thin film system

Based on the evidence discussed above and the combined measurements (TEM, EDS etc) on the system, the data about the film growth, as a result of interfacial reaction and phase transformation, is listed in Table4.3.1 and a model for the interfacial reactions of the thin

film system induced by interdiffusion is constructed as shown in Fig.4.3.11.



Fig.4.3.10. (a) A cross section image of the film system deposited at 700°C with a 3 hours further annealing at 700°C. Larger, fewer and less continuity of crystallites are seen. A row of small grains appear in SiO₂ near the interface to the amorphous phase. (b) A HRTEM image along with an inset indicating that small crystal grains have precipitated from the amorphous matrix and appeared adjacent to the Sr(Fe,Si)₁₂O₁₉ phase. (c) EDS spectra from the crystalline grain adjacent to Sr(Fe,Si)₁₂O₁₉.

	Thickness of individual layer in the film system		
Deposition and heat treatment	In the SrFeO ₃ film		SiO_2 (µm)
condition	Crystal (nm)	Amorphous (nm)	(amorphous)
RT deposition. for 4 min.	31	15	1.14
700°C deposition for 4 min.	15	55	1.17
700°C deposition +700°C 1hr annl.	10	42	1.16
700°C deposition +700°C 3hr annl.	50	L	1.16

Table 4.3.1.	Summary of the	measurement	of the	film	thickness	under	deposition	and
heat treatmen	t conditions							



Fig.4.3.11. Schematic illustrations of the changes in film thickness and interface structure at different deposition and thermal treatment conditions. (a) RT for 4 minutes as deposited. (b) 700°C for 4 minutes as deposited. (c) 700°C as-deposited with 1 hour further thermal annealing at 700°C. (d) 700°C as-deposited with 3 hours further annealing at 700°C and (e) with 10 hours further annealing at 700°C.

(b) Description of the interfacial reactions of the system

(i) Interfacial reactions of the thin film system deposited at room temperature:

There is no interfacial reaction occurring at this stage. The interfacial structure is

described as SrFeO3(nanocrys)/SrFeO3 (amor)/SiO2 (amor)/Si(crys),

where the subscripts *nanocrys, amor and crys* denote nano-crystallites, amorphous and crystalline forms, respectively.

(ii) Interfacial reactions of the thin film system deposited at 700°C:

a. In the as-deposited system, simultaneous film deposition and diffusion resulted in the reaction $SrFeO_{3(nanocrys)} + SiO_2 \rightarrow (Sr-Fe-O-Si)_{amor}$.

The interface structure is described as

 $SrFeO_{3(nanocrys)}[(SrFeO_3)_{[111]} + (SrFeO_3)_{[112]}] / (Sr-Fe-O-Si)_{amor} / SiO_2 / Si.$

b. In the system annealed at 700°C for 1 hour, elemental redistribution between

 $SrFeO_{3(nanocrys)}$ and $(Sr-Fe-O-Si)_{amor}$ resulted in a phase transformation and separation forming an interface of $Sr(Fe,Si)_{12}O_{19} / (Sr_{(rich)}-Fe-O-Si)_{(amor)}$. The reaction is described as $SrFeO_{3(nanocrys)} + (Sr-Fe-O-Si)_{amor} \rightarrow Sr(Fe,Si)_{12}O_{19} + (Sr_{(rich)}-Fe-O-Si)_{(amor)}$.

c. Further annealing (2-10 hours at 700°C) resulted in the crystal growth of $Sr(Fe,Si)_{12}O_{19}$, formation of nano-sized SrO_X crystallites in the $(Sr_{(rich)}-Fe-O-Si)_{(amor)}$ amorphous phase and interdiffusion between SiO₂ and the film. The sum of the reactions are described as

 $Sr(Fe,Si)_{12}O_{19(smaller crys.)} + (Sr_{(rich)}-Fe-O-Si)_{(amor)} + SiO_2 \rightarrow Sr(Fe,Si)_{12}O_{19 (larger crys.)} + SrO_X + an unidentified phase (in the SiO_2 region).$

Note all the above equations describing the interfacial reactions are unbalanced with respect to elemental compositions.

4.4. Conclusions to the SrFeO₃/SiO₂/Si system

There were no interfacial reactions observed in the SrFeO₃/SiO₂/Si system deposited at room temperature. The SrFeO₃ film was characterized as a layer of nano-sized crystal

domains with a layer of an amorphous phase of the same elemental composition adjacent to the SiO₂/Si substrate. The amorphous phase is not considered to exist as a result of interfacial reaction between $SrFeO_3$ and SiO_2 , since its composition is identical to the SrFeO₃ film. No preferential orientation occurs. When deposited at 700°C for 4 minutes, the SrFeO₃ film of the SrFeO₃/SiO₂/Si system exhibited a double phase (layered) structure. This included a layer of crystalline grains with preferential orientations [111] and [112] perpendicular to the surface, and a layered amorphous phase containing Sr, Fe, O with additional silicon. Following annealing at 700°C for 1 hour, the crystalline SrFeO₃ layer transformed to a hexagonal phase $Sr(Fe,Si)_{12}O_{19}$ with the lattice parameters a and c identical to the known compound $SrFe_{12}O_{19}$ but with additional Si, and leaving an amorphous layer comprising strontium, iron and silicon adjacent to it. Longer period annealing resulted in an increased growth of the previously identified crystalline phase $Sr(Fe,Si)_{12}O_{19}$ and additional crystallization within the amorphous region of the film forming crystalline grains with composition identified as SrO_X. The existence of SiO₂, as a buffer layer on the silicon substrate, promoted the formation of amorphous phases in the film at the SrFeO₃ / SiO₂ interface and was the source of thermal diffusion of silicon into the perovskite thin film. Consequently, SiO₂ is not a suitable choice of material for a diffusion barrier to construct stable SrFeO₃ thin film gas sensors for silicon based MEMS structures which require operation at elevated temperatures.

Chapter 5

Thermal Stability of SrFeO₃/Al₂O₃ Thin Films: TEM Study of Interfacial Reactions and Conductometric Sensing Response

5.1. Introduction

SrFeO_{2.5+x} materials can be used as thin film gas sensors ^[1, 8, 9,11] at a temperature 400 < T $< 600^{\circ}$ C since the reversible uptake of oxygen can only readily occur at this temperature range resulting in compositional change accompanied by significant changes in electrical conductivity which can then be monitored as the sensor transduction signal. The electrical and gas sensing properties of films of these material types are strongly dependent on the cation and oxygen stoichiometries ^[9] and film morphology.^[177-180] Examples have shown that films exhibit no crystallinity or texture cannot easily and reversibly transform from the brownmillerite to the cubic perovskite structures and consequently show limited sensor functionality. ^[181, 182] SrFeO_{2.5+x} thin film gas sensors typically have high sensitivity and rapid response to the changes of analyzed gas concentration at around 500°C. Hence, the SrFeO_{2.5+x} thin films together with the substrate have to withstand such an elevated temperature and to be durable at these temperatures in order to maintain long term sensor functionality. However, the perovskite materials may be unstable under certain thermochemical conditions ^[18] or at elevated operating temperatures. For example, in some ceramic-based gas sensors the films may react with the underlying substrate.^[19-25] Variations in microstructure and chemical composition of the thin film could result failure in signal production. The study described in the previous chapter "TEM investigation on the thermal stability of the SrFeO_{2.5+x}/SiO₂/Si system" ^[183] indicates that significant changes take place in the internal structure of the thin film systems due to interfacial reactions and elemental diffusion during the deposition and thermal treatment. Therefore, thermal stability of a sensing thin film system, in terms of potential interfacial reactions, must be taken into account in sensor design in order to ensure longer term signal reproducibility. Thus, investigate of crystal structure of the sensing film and thermal stability of thin film system is essential.

The evaluation of the thermal stability of $SrFeO_3$ /Al₂O₃ thin film is in light of the high thermal stability of Al₂O₃. Single crystal sapphire Al₂O₃ (hexagonal-rhombohedra a =0.4765 nm. c = 1.300 nm) has relatively high thermal conductivity, extreme electrical nonconductivity, volume resistivity (also known as specific insulation resistance. It is numerically equal-to the direct current resistance between opposite faces of a one centimeter cube of the material, expressed in ohm-centimeters.), hardness, wear resistance as well as a high upper use temperature. Its high thermal stability allows it to be used at far higher temperatures than most oxide materials (see table 5.1). There is no doubt that sintered Al₂O₃, on the other hand, possesses similar properties, such as thermal stability, to those of sapphire, but isotropic due to its random orientated grains. Further more, manufacturing of sintered Al₂O₃ is much more cost-efficient than sapphire. Although Al₂O₃ has long been taken as a preferred material for thin film substrate in high temperature devices including sensing devices, the evaluation of the thermal status of the thin film system at high temperature has been ignored. In this chapter, thin films $SrFeO_3$ have been grown onto single crystal and sintered polycrystalline Al₂O₃ by pulsed laser deposition (PLD) techniques for investigation of interfacial reactions using transmission electron microscopy (TEM). The films have been prepared under different growth conditions and subjected to post-deposition thermal treatments.

Physical Properties				
Chemical Formula	Al ₂ O ₃			
Structure	hexagonal-rhombohedral			
Molecular weight	101.96			
Lattice Constants Å	a=4.765, c=13,000			
Density (g/cm3)	3.98			
	9 Mohs.			
Hardness	1800 knoop parallel to C-axis,			
	2200 knoop perpendicular to C-axis			
	379 at 30° to C-axis			
	352 at 45° to C-axis			
Young Modulus (Gpa)	345 at 60° to C-axis			
	386 at 75° to C-axis			
Shear Modulus (Gpa)	145			
Bulk Modulus (Gpa)	240			
Bending Modulus / Modulus of Rupture	350 to 690			
(MPa)				
Tensile strength (MPa)	400 at 25°C, 275 at 500°C, 345 at 1000°C			
Elastic Coefficients	C11=496, C12=164, C13=115, C33=498,			
	C44=148			
Apparent Elastic Limit (MPa)	448 to 689			
Flexural Strength (GPa)	2.5 - 4.0			
Poisson ratio	0.25 - 0.30			
Friction Coefficient	0.15 on steel, 0.10 on sapphire			
Abrasion resistance	8 times higher than steel			

Table 5.1. Properties of sapphire Al₂O_{3.} (optical properties are not included)

(to be continued)

Thermal Properties			
Melting Point (°C)	2040		
Maximum use temperature (°C)	1800		
Specific Heat J/(kg × K)	105 at 91 K, 761 at 291 K		
Thermal coefficient of linear expansion	$6.66 \times 10-6$ parallel to optical axis,		
at 323 K (K-1)	$5 \times 10-6$ perpendicular to optical axis		
Thermal conductivity (W/m °K)	at 20° C 41.9		
Thermal Expansion (20 - 1000°C)	parallel to C-axis: 9.03 × 10-6°C		
	perpendicular to C-axis: 8.31 × 10-6°C		
	60° to C-axis: 8.4 × 10-6°C		
Electrical Properties			
Resistivity, Ohm·cm	at 20-500° C 1011 - 1016		
Dielectric Constant	11.5 parallel to C axis,		
	9.4 perpendicular to C axis		
Dielectric strength (V/cm)	4 × 105 Loss Tangent 10-4		
Stability Parameters			
In water	insoluble		
In HNO ₃ , H2SO ₄ , HCl, HF	insoluble up to 300° C		
In alkalis	insoluble up to 800° C		
In melts of metals: Mg, Al, Cr, Co, Ni,	insoluble up to 800 - 1000° C		
Na, K, Bi, Zn, Cs			
Radiation	no change in transmission above 2.5 micron		
	after exposure to 107 Rads. No visible		
	coloration after exposure to 108 Rads/hr for		
	60 minutes at -195° C		
Proton radiation	no change in transmission below 0.3 micron		
	after exposure 1012 proton/cm2 total dose.		

Table 5.1. (continued) Properties of sapphire Al₂O_{3.} (optical properties are not included)

Sintered Al_2O_3 was chosen as one of the substrates because it is a cost-effective alternate to single crystal alumina. Film structures were examined on the thin film systems grown at ambient temperature (RT) and 700°C. Characterization of interfacial reaction and phase transformation were realized on samples of the thin film system after additional annealing at 850°C and 1000°C. Analytical transmission electron microscopy including high resolution imaging, electron diffraction and energy dispersive spectrometry were utilized in the characterization. In parallel, an evaluation of the conductometric sensing functionality of the films was conducted on those grown at 700°C.

5.2. Experimental Procedure

5.2.1. Material preparation

(a) The target material for SrFeO₃ deposition

Target material for $SrFeO_3$ deposition is the same as the one used for $SrFeO_3/SiO_2/Si$ system (see Chapter 4, section 4.2.1).

(b) The substrates: Single crystal $(1\overline{1}02)$ alumina and sintered polycrystalline alumina were used as the substrates, with a size of 1cm x 1cm.

5.2.2. Pulsed laser deposition (PLD) condition

The SrFeO₃ pellet was then used as the target material for the deposition of SrFeO₃ thin films by the pulsed laser deposition (PLD) technique. The same excimer laser Lambda Physik LPX305i, Kr/F (λ =248nm), used for the SrFeO₃/SiO₂/Si was utilized for SrFeO₃/Al₂O₃ deposition. During deposition, the temperature of the substrate was maintained at either room temperature (RT~22°C) or 700°C. The films were deposited

for 4 minutes and 20 minutes at a laser pulse rate of 8Hz, pulse duration of 25ns, fluence of $\sim 1.5 \text{ J.cm}^{-2}$ and under a background oxygen pressure of 100 mTorr respectively.

5.2.3. Post deposition thermal annealing

Post thermal annealing for samples were carried out in a tube furnace with controlled gas flow. Annealing temperatures were chosen based on the purpose of the study for each thin film system. Heating of the samples was performed in air. The overall deposition and thermal heat treatment conditions for the samples studied in this chapter are listed in table 5.2.3.

Thin film system	Deposition	Annealing		
	°C / min.	Heating (°C / hr.)	Cooling	
SrFeO ₃ /Al ₂ O ₃ (Sapphire)	RT / 04			
SrFeO ₃ /Al ₂ O ₃ (Sapphire)	700 / 20			
SrFeO ₃ /Al ₂ O ₃ (Sapphire)	700 / 20	700 / 10	with furnace, in air	
SrFeO ₃ /Al ₂ O ₃ (Sapphire)	700 / 20	700 / 10 + 850 / 05	pressure N ₂	
SrFeO ₃ /Al ₂ O ₃ (Sapphire)	700 / 20	700 / 10 + 1000 / 05	pressure N ₂	
SrFeO ₃ /Al ₂ O ₃ (sintered)	RT / 04			
SrFeO ₃ /Al ₂ O ₃ (sintered)	700 / 20			
SrFeO ₃ /Al ₂ O ₃ (sintered)	700 / 20	700 / 10	pressure N ₂	
SrFeO ₃ /Al ₂ O ₃ (sintered)	700 / 20	700 / 10 + 850 / 05	pressure N ₂	

Table 5.2.3. List of specimens with deposition and thermal treatment conditions.

5.2.4. TEM specimen preparation

Cross section and plan view specimens of the $SrFeO_3$ films on the single crystalline Al_2O_3 (sapphire) and sintered Al_2O_3 substrates were prepared respectively for TEM

examination. Detailed procedures of cross-section and plan view TEM specimen preparation are described in Chapter 3. Since Al_2O_3 is extremely hard and brittle, removal of substrate by mechanical grinding and sputtering and handling of the specimens were difficult. Traditional methods described in chapter 3 are no longer optimum. Great care has to be taken and modified sample preparation method was created based on the idea of reducing sputtering to decrease the effect of preferred sputter rate between SrFeO₃ and Al₂O₃. To realize this the specimen was ground and polished using polishing pad with abrasive diamond from 9 micron to 0.25 micron to make a wedge shape in cross-section (< 15°) leaving the edge at the interest area (Fig. 5.2.4). The specimens were then Ar-ion sputtered at an angle <10° for about 1 hr at 4kv. For the specimen with multilayered film, the specific layers were accessed by incremental steps of Ar-ion sputtering to remove the upper layers by Ar-ion sputtering. A Gatan PIPS system was used for specimen sputtering.



Fig. 5.2.4. A wedge shaped specimen indicating that the area of interest is located at the edge of the specimen.

5.2.5. Thin film structure characterization using analytical TEM

Thin film structure characterization was realized by analytical transmission electron microscopy with the same equipment used for the characterization of SrFeO₃/SiO₂/Si system- the Philips CM20 equipped with an energy dispersive x-ray spectrometer: INCA

Energy TEM 200 and a Gatan UltraScan 1000 CCD camera. An accelerating voltage of 120 - 200kV was selected based on the purpose of each characterization. 200kV accelerating voltage was used to obtain higher beam energy for HRTEM imaging and lower voltage for diffraction. Beam size as small as less than 10nm was used for EDS chemical composition analysis across thin film thickness. Bright field (BF), dark field (DF) image and electron diffraction (ED) including convergent beam electron diffraction (CBED) techniques were used to investigate the crystallographic and interfacial structures of the films.

5.2.6. Test of conductometric sensing response

Conductivity and sensing testing of the $SrFeO_3$ / Al_2O_3 film systems were carried out using a two-wire method. The principle and detailed experimental procedures have been described in section 3.5 of chapter III.

5.3. Results and Discussion

5.3.1. Interfacial structure of SrFeO₃/Al₂O₃ system deposited at room temperature (a) SrFeO₃ thin film deposited onto sintered Al₂O₃ substrate

Structures of SrFeO₃ thin films deposited onto sintered Al_2O_3 substrates at RT and 700°C for 4 minutes respectively have been characterized. The structure of the SrFeO₃/Al₂O₃ (sintered) sample deposited at RT for 4 minutes is shown in the TEM micrograph of a cross section specimen (Fig. 5.3.1a). The thickness of the film is 56nm. The film has a columnar structure with each column consisting of nano-scaled grains shown in Fig.5.3.1b.

Columnar structures are often reported for thin film growth at low temperature. Typically, the overall morphology of the film is dramatically affected by the deposition temperature. Low temperature is in favor of nucleation of the film, on the other hand, at low temperature, limited migration or diffusion of the deposited species constrains the crystal growth laterally but facilitates the growth vertically during the deposition. As a result, a fine columnar structure is formed with a high density of crystal defects, pores and consequent weaker adhesion to the substrate. X-ray diffraction (XRD) patterns for these films show low intensity and broadened peaks which could be interpreted as being produced by an amorphous phase. However, the HRTEM image shown in Fig 5.3.1b supports the existence of morphology of nano-crystalline grains.

Notches on the surface of the substrate in the cross section image shown in Fig. 5.3.1a are due to pores that exist at the junctions of the grains in the sintered Al_2O_3 . Although the


(a)



Fig.5.3.1. (a) $SrFeO_3$ thin film deposited on sintered Al_2O_3 substrate at room temperature showing a columnar feature of the film and a gap between the film and the substrate indicating a poor film adhesion to the substrate. (b) A HRTEM image of the column featured film indicating that the columns in the film consist of nanocrystalline grains.

film lies on the substrate along the profile of the surface, gaps between film and substrate are visible as shown in Fig. 5.3.1a, again indicating a poor film adhesion.

(b) $SrFeO_3$ thin film deposited onto the single crystalline Al_2O_3 (sapphire) substrate

SrFeO₃ film deposited on the single crystalline Al₂O₃ (sapphire) substrate at room temperature demonstrates such poor adhesion to the substrate that obtaining a crosssection TEM image was impossible due to the separation of the film form the substrate unlike the case of the sintered Al_2O_3 substrate in which film can be held on the surface even though gaps are exist between the film and the substrate. This is because at low temperature the substrate provides less energy for deposited species to overcome the energy barrier in residing on the substrate surface for nucleation and growth, high density of defects must have generated at the interface. As a result a weakened interface formed. Compared with the thin film system with single crystalline Al_2O_3 , the film adhesion for the system with sintered substrate seems to be better; this is because the grain boundaries in the sintered alumina intersect the surface leaving defects such as boundaries between two grains, pits at the joint point of three boundaries. And the film by PLD completely cover the surface (see Fig. 5.3.1a), thus, such a "rough" surface provides favorite place for film to "grasp" increasing mechanical strength to hold the film on the substrate surface. However, films deposited onto the sintered alumina still weakly attach to the substrate because of gaps occurring at the interface as seen in Fig. 5.3.1a. Low temperature deposition is the main reason for film having poor adhesion to the substrate.

5.3.2. Interfacial structure of SrFeO₃/Al₂O₃ system deposited at 700°C

127

(a) SrFeO₃ thin film deposited onto the single crystalline Al_2O_3 (sapphire) at 700 °C for

4 minutes

The interfacial structure of SrFeO₃ /Al₂O₃ (sapphire) system grown at 700°C for 4 minutes is shown in the TEM images of Fig.5.3.2. The average thickness of the SrFeO₃ film is 38nm. The film is made up of grains with boundaries perpendicular to the substrate. These features are shown in more detail in Fig.5.3.2a. Each grain contains subgrains which can be identified by contrast difference in a BF image and from the lattice fringes (Fig 5.3.2b) which indicate the associated orientation and interplanar d-spacings. At the interface between the SrFeO₃ and Al₂O₃, as shown in the HRTEM image in Fig.5.3.2c, some atomic scaled Al₂O₃ lattice steps are present which is believed to be a form of surface defect. No evidence about interface interdiffusion reaction has been found meaning that interfacial reaction doesn't occur at this stage.

In the image of a plan view specimen shown in Fig.5.3.2d, the SrFeO₃ grain size in the layer is about 40nm. EDX analysis (Fig.5.3.2e) of the film indicates that the elemental composition corresponds to that of the target used in the PLD step, confirming congruent transfer during growth (note the Cu peak in the spectrum is due to copper being present in the TEM specimen support). The SA electron diffraction patterns (EDP) shown in Fig.5.3.2f, represent a combination of reflections from the single crystal Al₂O₃ substrate and a set of diffraction rings due to the SrFeO₃ thin film. The diffraction patterns were identified as being due to the phase SrFeO_{2.97} (PDF file ID No. 40-0905, cubic $a_0 = 0.3855$ nm) and are indexed as shown in the figure. Interpretation of the ED patterns also shows no evidence of any preferential orientation of the crystalline film.





Fig.5.3.2. (a-d)) TEM micrograph of a cross section sample of the SrFeO₃ thin film deposited onto the sapphire (single crystal Al_2O_3) substrate at 700°C for 4 minutes. (a) BF image of a cross section specimen. (b) A BF TEM image showing the sub-grains in the film. (c) A HRTEM image of a cross section specimen showing the surface of the Al_2O_3 substrate at the interface. (d) A BF TEM micrograph from a plan view specimen showing the morphology of the film. (To be continued)



Fig. 5.3.2. (continued) (e) EDX spectra indicating that the elements contained in the film are the same as those in the target (peak at 8.04kev is Cu from specimen copper ring). (f) Indexed SA diffraction patterns from the film shown in (d) indicating that it is the phase known as $SrFeO_{2.97}$.

(b) SrFeO₃ thin film deposited onto sintered Al_2O_3 at 700 °C for 4 minutes

Shown in Fig.5.3.2g is a cross section of the $SrFeO_3/Al_2O_3$ (sintered) thin film system grown at 700°C for 4 mininuts. The thickness of the $SrFeO_3$ film is 60 nm, and it consists of a single row of grains, normal to the substrate and with similar geometry to films deposited onto the single crystalline Al_2O_3 substrate at the same temperature. Also, it is demonstrated by ED that the crystal structure of the $SrFeO_3$ films is identical to that deposited onto single crystal Al_2O_3 under the same conditions. The film in the $SrFeO_3/Al_2O_3$ (sintered) system exhibits an excellent conformation to the rough Al_2O_3 surface, with a uniform film thickness and good adhesion. This is in contrast to $SrFeO_3$ deposited onto sintered Al_2O_3 at room temperature, as shown in Fig.5.3.1a. It clearly indicates that higher deposition temperature improve film adhesion to the substrate.



(g)

Fig. 5.3.2g. A BF TEM cross-sectional image of the $SrFeO_3/Al_2O_3$ (sintered) system showing the morphology of the film a complete film covering over the substrate and good adhesion to the substrate.

5.3.3. Interfacial structure of SrFeO₃/Al₂O₃ system deposited 700°C for 20 minutes and further annealing at 700°C for 10 hours

The purpose of a longer deposition time for this system is to obtain a thicker film for the further film and interfacial characterization after annealing at higher temperature. Films of SrFeO₃ deposited onto single crystal and sintered Al_2O_3 substrates at 700°C for 20 minutes produce a thicker film, (~ 287nm) and these have been studied to examine effects due to longer term thermal annealing with subsequent interfacial characterization. Shown in Fig. 5.3.3a is the cross-sectional image of the SrFeO₃/Al₂O₃ (sapphire) system



(a)



(b)

Fig.5.3.3. (a) a cross section image of the $SrFeO_3/Al_2O_3$ thin film system deposited at 700°C for 20 minutes and annealed at 700°C for 10hrs. (b) A plan view image of the $SrFeO_3$ thin film. (To be continued)



(c)



Fig.5.3.3 (continued). (c) An indexed electron diffraction pattern and (d) the EDS spectra from the area shown in (b) indicating that the film remains $SrFeO_3$ after 10 hrs annealing at 700°C.

annealed at 700°C for 10 hours in air. The film contains a single layer of film with multiple crystalline grains (Fig. 5.3.3b, c). Except for having a larger grain size than the one shown in Fig.5.3.2a due to the longer term annealing, the interfacial structures and chemical composition remain the same as $SrFeO_3$ which are proved by ED and EDS analysis (Fig.5.3.3c and d), implying that the interfaces of the both thin film systems are thermally stable under these conditions.

5.3.4. Interfacial structure of SrFeO₃/Al₂O₃ system annealed at 850°C for 5 hours after annealing at 700 for 10 hours

Further annealing at higher temperature was conducted in order to investigate the limit of interface thermal stability of the SrFeO₃/Al₂O₃ thin film systems. Interfacial reactions began to be observed after additional annealing at 850°C for 5 hours (i.e. 700°C for 10 hours plus 850°C for 5 hours). Shown in Fig. 5.3.4a and b are the SrFeO₃ thin films on single crystal and sintered Al₂O₃ substrates respectively, where interfacial reactions have occurred. At the interface, shown in Fig. 5.3.4a, the grains grow into the Al₂O₃ substrate and this penetration results in a zigzag shaped boundary. The products of the interfacial reaction are visible in the HRTEM image. The grains adjacent to the film, shown in Fig.5.3.4b, are elongated and oriented along the interface. This region is identified as consisting of a new phase due to the interfacial reaction. Fig. 5.3.4c also shows that the zigzag shaped boundary contains sections of the interface at specific orientations. Obviously, an interface represented by a zigzag shaped boundary between two phases is larger in surface area than a flat interface. However, the appearance of this type of interface implies that the zigzag shaped boundary must have lower interface energy than





Fig.5.3.4. (a) A BF TEM image of the $SrFeO_3/Al_2O_3$ (single crystalline) system deposited at 700°C for 20 min and annealing at 850°C for 5hrs after annealing at 700°C for 10hrs, and (b) $SrFeO_3/Al_2O_3$ (sintered) system with the same process condition as in (a) showing the initial interfacial reaction forming new phases. (c) A HRTEM image at the interface of $SrFeO_3/Al_2O_3$ (single crystalline) showing that the new phase penetrates the Al_2O_3 substrate forming a zigzag-shaped interface.

a flat interface does. To realize this, the sections of interface must be orientated in such a way that the sectional interface possesses low energy. This type of interface likely has maximum coincident lattice sites shared by both crystalline phases adjacent at the interface. Further confirmation of this statement is not done because of the difficulty of determination of exact orientations of the interface sections.

A quantitative analysis on the interface products is not possible due to a limited quantity of the new phases at the interface. Conclusive phase identification was not determined at this stage. However, EDS analysis showed that the phase contains additional elemental Al and with Sr/Fe < 1 compared to $SrFeO_3$. The ED pattern also showed extra weak diffraction rings compared to $SrFeO_3$. Clearly, this is evidence that one or more new phases are forming at the interface at this stage of annealing.

However, based on data discussed below, there are two phases likely to form at the interface; one is a $SrAl_2O_4$ type and the other is a $SrFe_{12}O_{19}$ type of compound. The phase present at the interface adjacent to Al_2O_3 is likely $SrAl_2O_4$, an assessment supported by comparing the experimentally measured d-spacing (d = 0.2579nm) with the powder diffraction database value for $SrAl_2O_4$, $d_{[002]} = 0.2554nm$, [PDF# 34-0379]. Other supporting evidence is addressed in a later section.

5.3.5. Interfacial structure of the SrFeO₃/Al₂O₃ system annealed at 1000°C for 5 hrs after annealing at 700°C for 10 hours

(a) Morphological structure of the thin film system

Further quantitative identification of the interfacial reaction features was determined on the sample annealed at 1000°C for 5 hours, following prior annealing at 700°C for 10 hours. Shown in Fig. 5.3.5a is a cross section BF TEM micrograph of this thin film system. The thin film structure consists of a top layer and mid-layer. The morphology of them is different and is readily distinguished. The top layer possesses less contrast. Both layers have uneven thickness, the thickness of the top layer ranges from 124 to160nm; the mid-layer from 290 to 400nm. The mid-layer contains zones filled with bunch of parallel oriented grains Individual layers of the film are isolated and the plan view images of the top and mid- layers are shown in Fig 5.3.5b, and c, respectively. It is interesting to see that the grain size for top layer (Fig.5.3.5b) is about the same size as that of zones in the mid-layer shown in Fig. 5.3.5c, and each grain in the top layer covers a zone in the mid-layer. Within a zone in the mid-layer, shown in Fig. 5.3.5c, the features are similar to that of a zone shown in the cross section image (Fig.5.3.5a), indicating that a zone is formed by stacking a number of parallel-sided slab-like grains. Shown in Fig. 5.3.5d is a plan view of an area in the topmost layer. This shows a mixture of a barshaped phase identical to those in the top layer shown in Fig. 5.3.5b, and the zones of the mid-layer phase as shown in Fig.5.3.5c. This implies that the mid-phase has grown to the outermost surface.

(b) Phase identification of the thin film system

Phase identification in the region of the top layer was realized by applying ED combined with EDS and HRTEM image analysis. The crystallographic phase information was obtained using the convergent beam electron diffraction (CBED) technique, and the



(a)



Fig. 5.3.5. BF TEM micrographs of the thin film system annealed at 700°C for 10 hours followed by annealing at 1000°C for 5 hours. (a) An image of a cross-section specimen consisting of an outermost layer and a mid-layer which adjacent to the substrate Al₂O₃. (b) A plan-view micrograph of the individual top layer, and (c) the mid-layer with parallel-sided slab-like grains. (d) A plan view of an area in the outermost surface showing a mixture of the phases in (b) and (c) indicating that the mid-layer has grown into the outermost surface by consuming the phase shown in (b). (To be continued)

CBED pattern is shown in Fig. 5.3.5e along with the zero order Laue zone (ZOLZ) reflections (the inset in Fig. 5.3.5e). The first order Laue zone (FOLZ) reflections are present as a high intensity circle in Fig. 5.3.5e and individual reflections in Fig. 5.3.5f. The ZOLZ gives the two-dimensional information about the lattice, and the FOLZ pattern is then used to derive the third dimensional information about the lattice based on the equation 3.2 and 3.3. A d-spacing of d = 0.522nm is derived from the ZOLZ reflections shown in Fig. 5.3.5e, and the distance between the ZOLZ and the FOLZ is calculated to be $H^* = 0.437$ (1/nm) reflecting an interplanar distance H = 2.290nm. ($H = 1/H^*$) where H^* is the distance between ZOLZ and HOLZ (including FOLZ) in reciprocal lattice, and H is the corresponding interplanar in the real crystal lattice.

The next step in phase identification by ED is to determining the crystal type. Symmetry analysis on the CBED pattern shown in Fig 5.3.5e and f gives the observed symmetry of ZOLZ *6mm*, the corresponding projection diffraction group it belongs to is $6mm1_R$. The symmetry information from HOLZ is also *6mm* which gives rise to the possible diffraction group $6mm1_R$ and 6mm for the diffraction pattern according to the table 5.3.5a,^[184] suggesting possible space groups 6mm and 6/mmm, respectively (table 5.3.5b).^[185] Conclusive point group determination needs at least another CBED pattern for more symmetric information but it is not necessary at this moment for a conclusive crystal system determination because both above mentioned diffraction groups give an identical crystal system-hexagonal (see table 5.3.5b), thus aiding lattice parameter determination. As a result, a hexagonal unit cell is determined for the new phase with, a = 0.603nm, c = 2.290nm. Note, *a* is calculated using the equation $a=2d \tan (\pi/6)$.



(e)



Fig.5.3.5. (continued) CBED patterns taken from the outmost layer of the specimen shown in (b). (e) A CBED pattern consisting of a FOLZ reflection ring and ZOLZ reflection discs (inset) and fold a 6 symmetric information about the ZOLZ can be obtained. (f) A CBED pattern showing the reflection discs of both ZOLZ and FOLZ. 4 lines cross the reflections in the FOLZ and intercept at joints overlapping with the reflections in ZOLZ indicating that the whole pattern has at least 6 fold symmetry element plus a mirror symmetry element at the zone direction. The phase is determined to be a SrFe₁₂O₁₉ type of phase. (To be continued)

Observed	Projection	Possible	Symmetries of high-order information						
zero-order zone	group	groups	whole pattern	zero-order disk					
1	1 _R	1	1	1					
		1 _R	1	2					
		2	2	2					
2	21 _R	2 _R	1	1					
		21 _R	2	2					
		m _R	1	m					
m	$m1_R$	m	m	m					
		$m1_R$	m	2 <i>m</i>					
		$2m_{\rm R}m_{\rm R}$	2	2 <i>mm</i>					
2	2	2mm	2 <i>mm</i>	2mm					
2mm	2mm1 _R	$2_{R}mm_{R}$	m	m					
		$2mm1_R$	2 <i>mm</i>	2 <i>mm</i>					
4		4	4	4					
	41 _R	4 _R	2	4					
		41 _R	4	4					
		$4m_{\rm R}m_{\rm R}$	4	4 <i>mm</i>					
A	A	4mm	4 <i>mm</i>	4 <i>mm</i>					
4 <i>mm</i>	$4mm_{\rm R}$	$4_{R}mm_{R}$	2 <i>mm</i>	4 <i>mm</i>					
		$4mm1_R$	4mm	4mm					
•	21	3	3	3					
3	31 _R	31 _R	3	6					
		3m _R	3	3m					
3 <i>m</i>	$3m1_{R}$	3m	3 <i>m</i>	3m					
		3 <i>m</i> 1 _R	3m	6 <i>mm</i>					
		6	6	6					
6	61 _R	6 _R	3	3					
		61 _R	6	6					
		$6m_{\rm R}m_{\rm R}$	6	6mm /					
6	6mm1_	6 <i>mm</i>	6 <i>mm</i>	6 <i>mm</i>					
Unun	Unit IR	6 _R mm _R	3m	3 <i>m</i>					
		6mm1 _R	бтт	бтт					

Table 5.3.5a Relation between the observed symmetries in CBED patterns and the 31 diffraction groups which correspond to the 32 different three-dimensional point group^[184]

			1	1 _R	2	2_{R}	21 _R	mR	3	mlR	2m _R m _R	2mm	2 _R mm _R	2mm1 _R	4	48	41 _R	4m _R m _R	4 <i>mm</i>	4 _R mm _R	4mm 1 _R	3	6 ^R	3mr R	3177	6 _R mm _R	6	31 _R	61 _R	6m _R m _R	6mm	3m1 _R	6mm1 _R
	1	۲ ۲	×															_				_							_				Η
	ī	1			Η	×						Π	Н							Η						-					Π		П
	2	Z	×	-	×	-		×	-	\vdash			-	-	Η	-	Н	-		-			Н	_	-		-	Η			Η	_	-
	* m	- -	×	×					×								_					_		-		_			-		Η		
	2/m	X				×	×					-	×				-	_		Η				-					-				
	222	0	×					x			×														Η							_	Π
	mm2	0	×					×	×	×		×						-	_								Η		-				
	mmm	0				×			Π				×	×		-																	
	4	Te	×					×							×																		
	i	Te	×					×								×																	
	4/ <i>m</i>	Te		•		×							×				x													•			
	422	Te	×					x			×							×															
3	4mm	Te	×					×	×	×									×														
stal	4 2 <i>m</i>	Te	×					x	×	×	×									×													
Poin	4/ <i>mm</i>	r H				×							×	×							×												
g	3	3 L	×																			×											
ups	3	Τg				×																	×										
	32	ЗL	×		×			×																×									
	3m	Tg	×	×					×																×								
	3m	3L				×	×						×													×							
	6	Η	×					×																			×						
	Ĝ	H	×						×											_								×					
	6/ <i>m</i>	H				×							×					_											X				
	622	H	×					×			×												-							×			
	6 <i>mm</i>	Ξ	×					×	×	×																	Ц				×		Ц
	6m2	H	×					×	×	×		×																			Ц	×	
	6/ <i>mm</i> n	<u>n I</u>	_			×							×	×	_													_					×
	23	0	×		$\left - \right $			×			×									\square	Ц	×					Ц	\vdash		\square	$\left - \right $		
	<i>m</i> 3	<u>_</u>			μ	×							×	×	μ				\square	\vdash	Ц		×						\square			-	\mid
	432	0	×			-		×	\square	Ц	×			Н	Ц		Ц	×	Н		μ		Ц	×	Н	Щ	H	\vdash	\square	Н	$\left \cdot \right $	Н	Н
	43m		×			-		×	×	×			\vdash	\vdash	Н		H			Ě	L				×					\vdash	\vdash	$\left - \right $	$\left \right $
	m3m	n				×							×	×							×					×							

Table 5.3.5b. relation between the diffraction groups and crystal point groups^[185]

Since the zone axis of the CBED pattern is parallel to the beam and perpendicular to the thin film surface, this unique orientation relationship makes it suitable for a HRTEM cross section image of the film to acquire supplementary information about the crystal structure. Shown in Fig. 5.3.5 g (left-side) is a HRTEM image taken from a plan view specimen along with a filtered image (Fig. 5.3.5g right-side) produced by fast Fouriertransform (FFT). The image is a translation of a hexagon with side length a = 0.603nm, which is in agreement with the result derived form the CBED pattern. Fig.5.5h is a HRTEM cross section image of the top layer showing a periodicity of an inter-planar spacing of 1.132nm, which is about half of the measured H from the CBED pattern, supporting the lattice structure determined by CBED. Fig.5.3.5i is the EDS analysis on the top layer indicating that the major elemental components in the phase are Fe and O and the minority elements are Sr with a trace of aluminum The known material which can best match this data is the phase $SrFe_{12}O_{19}$ (PDF #33-1340, Hexagonal a = 0.5886nmc = 2.3037nm), with the differences in lattice parameters between the measured and the proposed phase being 2.3% for a, and 0.5% for c. This mismatch in parameters may be due to variation of the relative elemental content (such as Al being present) which is not precisely in the ratio of Sr:Fe:O as 1:12:19. Thus, the formula of the phase is proposed as $SrFe_{12-v}Al_vO_{19}$.

Phase identification for the mid-layer was realized by micro-diffraction on many single grain zone. This approach was taken because each zone acts as a single crystal, a selected area for ED does not contain enough grains (i.e. zones) to produce a EDP with continuous rings.



Fig. 5.3.5. (Continued) (g) A HRTEM image (left-side) and its FFT treated image (rightside) of the $SrFe_{12}O_{19}$ -type of phase (the top layer). (h) A HRTEM image of the top layer of a cross-section specimen showing the periodicity in the lattice structure in the direction perpendicular to the film surface. (i) EDS spectra of this phase providing elemental information for the phase Sr, Fe, O and additional Al. (to be continued)



(j)





Fig. 5.3.5 (continued). (j) a HRTEM plan-view image of the mid-layer ($SrAl_2O_4$ type structure) demonstrating the interfacial relationship in a grain zone. (k) a representative EDP of the mid-layer ($SrAl_2O_4$ type structure). (l) EDS of the mid layer showing the elemental components Sr, Al₂O and additional Fe.

Table 5.3.5c. Comparison of d-spacings between the phase to be determined and phase $SrAl_2O_4$ (PDF#34-0379).

	d-			d-	
d-spacing of the	spacing	Selected	SrAl ₂ O ₄	spacing	Selected
phase measured	of	Intensity	Measured (cont')	of	Intensity
from the EDPs	SrAl ₂ O ₄			SrAl ₂ O ₄	
	(PDF#3			(PDF#3	
	4-0379)			4-0379)	
	, í			(cont')	
$6.104 (\pm 0.05) (5)$	6.0942			2.2241	
5.127	5.1527			2.2130	
$4.462 (\pm 0.04) (4)$	4.4465	52		2.2061	
4.379	4.4132			2.1956	
3.915	4.0186			2.1562	
3.874	3.9071			2.1414	
3.815	3.8523		$2.101 (\pm 0.015) (2)$	2.1067	
3.832	3.8022				
3.410					
$3.355 (\pm 0.05) (5)$	3.3508				
	0.0000		:	2.0102	
3 169	3.1415	100			
3.086	3.0481	91		1.9541	
	<u></u>				
$2.975 (\pm 0.04) (6)$	2.9836	76			
	2.2000				
			$1.928 (\pm 0.002) (2)$	1 9261	
2712(+0.02)(2)	2 6754			1.5201	
2 567	2 5754	33	1 870	1 8676	
2.567 2.545 (+ 0.01) (3)	2 5535	69	1.070	1.0070	
2.515 (= 0.01) (5)	2 5057		1 763		
2.161	2.5037		1 711		
	2.4323		1.684		
2 326	2.4246		1 661		
2.0.40	2.4093		1 628		
	2.3684			1.6028	
	2.3366			1.5975	
	2.3214		1 533	1.00710	
	2.5217		1.000		
	2.3366 2.3214 2.2577		1.533	1.5975	

Note: a d-spacing written as $x.xxxx (\pm 0.xx) (x)$, where the number in the first parenthesis is the range of errors. The number in the second parenthesis is the number of the diffraction patterns used for the calculation.

However, the parallel-sided slab-like grains in a zone introduce twin boundaries or small angle boundaries as the main crystal defects (Fig. 5.3.5j), which result in unusual single ED pattern. A representative EDP from a grain zone is shown in Fig.5.3.5k. It is apparent that diffraction streaks have resulted from an array of slabs that is lying inversely to the thickness of the slabs and having a small orientation difference. A series of d-spacings were obtained by taking EDPs from many grain zones (Table 5.3.5c), with which the d-spacings of the phase known as $SrAl_2O_4$ (PDF #34-0379, Monoclinic, a =0.8442nm b = 0.8822nm, c = 0.5161nm) is compared. Not only the spacings but also the intensities for the strongest diffractions have a good match with the known phase SrAlO₄. Thus, the Bravais lattice of the phase is determined to be of the SrAl₂O₄ type. However, information from the EDS analysis, shown in Fig.5.3.5l, indicates that the phase also contains some Fe, therefore the formula of the phase is suggested as SrAl_{2-x} Fe_xO₄. Fe is assumed to substitute for Al based on the consideration of matched valency in the compound and the closer ionic radius of Fe (0.0645nm) to Al (0.0535 nm) than to Sr (0.112 nm).^[186]

5.3.6. The chemistry of the SrFeO₃/Al₂O₃ interfacial reactions at 1000°C

The chemistry of the phase transformation, as a result of the formation of the new phases, is thus proposed using the following equations:

$$12Sr \ Fe \ O_3 = 11SrO + SrFe_{12}O_{19} + 3O_2$$
 5.1

Equation 5.1 is used to describe the initial phase transformation at the interface of $Al_2O_3/SrFeO_3$, where Sr is considered to be the diffusing element from SrFeO₃ to result in a new phase SrFe₁₂O₁₉. Note that in equation 5.1 the reactant SrFeO₃ could be replaced

by $Sr_2Fe_2O_5$ ($Sr_2Fe_2O_5 = 2 SrFeO_{2.5}$). It is the phase $Sr_2Fe_2O_5$ which is considered to involve in the reaction instead of $SrFeO_3$ ($SrFeO_{2.5+x} 0 < x < 0.5$). This is because $SrFeO_3$ is non-stoichiomitric in oxygen. The stoiciometry of oxygen changes with environmental pressure and temperature. Ordered oxygen atoms occupying octahedron positions in the lattice tend to be disordered at high temperature that ease oxygen atoms off the binding from Fe ions and release from the lattice at high temperature to form $SrFeO_{2.5}$ ^[11]. At high temperature it is more accurate for $SrFeO_3$ to be replaced by $Sr_2Fe_2O_5$ in describing the chemical reaction, therefore, reaction indicated by equation 5.1 can be simply written as

$$6Sr_2Fe_2O_5 = 11SrO + SrFe_{12}O_{19}$$
 5.2

Equation 5.2 is considered to be the initial phase transformation at the interface of $Al_2O_3/SrFeO_3$, where Sr is considered to be the diffusing element from SrFeO₃ to result in a new phase $SrFe_{12}O_{19}$. Accompanying this process, the further diffusion of Sr into Al_2O_3 proceeds as shown in equation 5.3

$$Al_2O_3 + SrO \Rightarrow SrAl_2O_4$$
 5.3

Thus, the additional phase forms, and a new interface structure is created, i.e., $Al_2O_3/SrAl_2O_4/SrFe_{12}O_{19}/SrFeO_3$. For simplicity, the additional interdiffusion of Fe and Al across the interface is not indicated in the equation, therefore, $SrAl_2O_4$ and $SrFe_{12}O_{19}$ represent the phases $SrAl_{2-x}Fe_xO_4$ and $SrFe_{12-y}Al_yO_{19}$ respectively. The overall reaction is given by combining the equations 5.2 and 5.3

$$11Al_2O_3 + 6Sr_2Fe_2O_5 = 11SrAl_2O_4 + SrFe_{12}O_{19}$$
5.4

5.3.7. Mechanism of phase transformation

(a) Characteristics of interfaces of the $SrFeO_3/Al_2O_3$ thin film system

Phase transformation occurs at interface by means of interfacial reactions due to elements diffusion. The growth front at the evolving interface can be found as shown in Fig.5.3.7a, a HRTEM image of the region between Al_2O_3 and $SrAl_{2-x}Fe_xO_4$. The $Al_2O_3/SrAl_{2-x}Fe_xO_4$ interface is outlined with a fractal line. The phase $SrAl_{2-x}Fe_xO_4$ penetrates the Al_2O_3 suggesting a crystal structure which is evolving from Al_2O_3 into $SrAl_{2-x}Fe_xO_4$ and with specific orientations between the adjacent phases. Shown in Fig.5.3.7b is HRTEM image of the region between the $SrAl_{2-x}Fe_xO_4$ and $SrFe_{12-y}Al_yO_{19}$. Unlike the fractal feature of the $Al_2O_3/SrAl_{2-x}Fe_xO_4$ interface, the $SrAl_{2-x}Fe_xO_4/SrFe_{12-y}Al_yO_{19}$ interface consists of parallel sections connected by atomic steps, which implies a different growth mechanism of $SrAl_{2-x}Fe_xO_4$ at this interface from that at the $Al_2O_3/SrAl_2$



Fig. 5.3.7 (a) A HRTEM image at the $SrAl_{2-x} Fe_xO_4 / Al_2O_3$ interface indicating a fractioned interface and crystal orientation relationship. (b) A HRTEM image showing the sectioned parallel $SrFe_{12}O_{19}/Al_2O_3$ interface and crystal orientation relationship between the two phases. (To be continued)

 $_{x}Fe_{x}O_{4}$ interface. The phase $SrFe_{12-y}Al_{y}O_{19}$ is considered to be consumed at the $SrAl_{2-x}Fe_{x}O_{4}/SrFe_{12-y}Al_{y}O_{19}$ interface during the growth of $SrAl_{2-x}Fe_{x}O_{4}$.

(b) Crystal orientation between the phases at the interfaces

The orientational relationship between the crystalline $SrAl_{2-x}Fe_xO_4$ growth and the Al_2O_3 substrate is determined by identifying the crystal planes represented by the lattice fringes. The angle between the (220) of $SrAl_{2-x}Fe_xO_4$ and (012) of Al_2O_3 is ~ 45° as shown in Fig. 5.3.7a. In the region of $SrAl_{2-x}Fe_xO_4$, the parallel-sided slabs are separated by small angled boundaries as shown in Fig.5.3.5j. The angle between the planes (220) of $SrAl_2$. $_xFe_xO_4$ and (001) of $SrFe_{12-y}Al_yO_{19}$ is also ~ 45° as shown in Fig.5.3.7b. This match in lattice geometric orientation is presumably governed by the system minimizing the interface energy.

5.3.8. Model of thin film evolution upon thermal treatment conditions

To further define the diffusion aspects of the interfacial reactions, a schematic illustration of the evolving interfacial structure of the $SrFeO_3/Al_2O_3$ thin film system after different thermal treatments is shown in Fig.5.3.8. Fig.5.3.8a represents the structure of the $SrFeO_3/Al_2O_3$ (sapphire) thin film system deposited at 700°C for 20minutes and annealed at 700°C for 10 hours, and where no interfacial reactions have yet initiated. Fig.5.3.8b represents the thin film system following additional annealing at 850°C for 10 hours. As a result of this thermal treatment, new phases now precipitate at the $SrFeO_3/Al_2O_3$ interface. Shown in Fig. 5.3.8c is the schematic structure of the thin film system with an additional annealing of 10 hours at 700°C and followed by a further annealing for 5 hours

at 1000°C. Fig.5.3.8c indicates the expanded depth of penetration of the new phases $SrFe_{12-x}Al_xO_{19}$ and $SrAl_{2-x}Fe_xO_4$ as both the Al_2O_3 substrate and the initial $SrFeO_3$ film are consumed.



Fig. 5.3.8. Schematic illustration of the evolution of the interfacial structure of the $SrFeO_3/Al_2O_3$ thin film system. (a) Interfacial structure of the thin film system deposited at 700°C and thermal annealing at 700°C for 10 hours. (b) Interfacial structure of the thin film system with thermal treatment at 700°C for10 hours plus 850°C for 5 hours. (c) Interfacial structure of the thin film system with thermal treatment at 700°C for10 hours plus 850°C for 5 hours.

5.3.9. Thermodynamics of interfacial reactions

The Gibbs function of a condensed phase is often discribed in terms of the enthalpy and entropy of the system:

$$\Delta G = \Delta H - T \Delta S \tag{5.5}$$

where G is the Gibbs free energy, H is enthalpy and S is entropy of the system. ΔG represents the change in Bibbs free energy after a system undergoes a process in which it moves from one thermodynamic state to another. Equation 5.5 is used to determine the the direction and limit of a reaction, an equilibrium state of a condensed crystalline system. At equilibrium the statement quantifies the competing tendencies of electrostatic and crystal field (bonding and order) versus entropy (or thermal energy and disorder). A balance is achieved and the structure is stable when $\Delta G = 0$.

In a multicomponent system at constant temperature and pressure, the change in Gibbs free energy of an individual phase due to an incremental change in the concentration of one component is defined as the chamical potential.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{i,P,n_j}$$
 5.6

Nonuniform composition or metastable phase development results in local energy gradients which are the driving forces behind the continuous trend of atomic movements toward the equilibrium state. A general differential statement of the Gibbs function of each phase for a multicomponent system is described as

$$dG = VdP - SdT + \sum_{i} \mu_{i} \delta n_{i}$$
5.7

where the final term is summed over all species. Each of the μ_i is the chemical potential of the component "*i*" and δn_i is the incremental change in composition of the phase in terms of that component. At constant temperature and pressure, the free energy balance can be stated using the expanded Gibbs equation for the components a, b, c,...

$$dG_{T,P} = \sum_{i} \mu_{i} \delta n_{i} = \mu_{a} \partial n_{a} + \mu_{b} \partial n_{b} + \mu_{c} \partial n_{c} + \dots$$
 5.8

Changes in the driving force are due to the composition changes to make transition go forward till dG = 0 at which

$$(\mu_i)_P = (\mu_i)_O = (\mu_i)_M = (\mu_i)_N = \dots$$
 5.9

where *i* is the component *a*, *b*, *c*, ... and *P*, *Q*, *M*, *N*... are the phases in a multicomponent system. This means that at equilibrium for a multiphase system, coexistence of compatible phases requires that each component in all of the present phases has the same chemical potential. As the chemical potential is dependent on phase composition (including defects), each phase in a multiphase system has their own composition range before equilibrium. All real materials contain solutes, (relative to the stoichiometric compound formula) and defects. A compositional range and the defects are the source of driving force for real processes in the approach to heterogeneous phase equilibrium. The driving force is the net energy available in the system to accomplish the work of transition. This work entails the physical motion of atoms and molecules, electronic transitions as bonding states are redistributed, and the work to create an interface between phases.

A thin film system (including the substrate) is a thermally unstable system. For example, in the field of physical metallurgy, a system of a carbon thin film deposited onto an iron substrate is not thermal stable at any temperatures but the solid solution of carbon in iron Fe[C] is, if the relative weight ratio of carbon (W_c) to iron (W_{Fe}) is less than the solubility limit of Fe[C], for example, at temperature $T=740^{\circ}$ C, i.e., the relative weight ratio W_c/(W_{Fe}+W_c) $\leq 0.025\%$, as illustrated by Fig. 5.3.9 a. In the dash-line defined rectangular region of the Fe-C diagram (see the enlarged diagram of this region shown in Fig. 5.3.9.b), α -Fe (solid solution of C in body-centered Fe lattice) existing in the single phase region pointed by an arrow possesses the maximum solubility of 0.025% C at 740°C, which implies that a Fe[C] solid solution with less than 0.025% C has minimum free energy if it is a single phase α -Fe. Otherwise, the system will not be in minimum energy state, (in other words, $dG \neq 0$), like the deposited C/Fe thin film system. The system will become thermal stable only when the carbon film completely resolves into iron and the system becomes a homogenous phase (Fe[C]) is

$$dG = \mu_{Fe} dn_{Fe} + \mu_C dn_C + \mu_{Fe[C]} dn_{Fe[C]}$$
5.10

where the subscripts Fe, C, and Fe[C] stand for the Fe element of the substrate, the C element of the carbon film and the solid solution of carbon in iron respectively. This process is realized by carbon diffusion at the interface Fe/C and kinetically depends on the temperature and time because thermal activation energy is needed to overcome the energy barriers to allow the atoms to move and new interface to generate. The higher the temperature the quicker the process will go. The concentration of C in Fe will reach its saturated level at the interface after a period of time depending on the diffusion coefficient of C in Fe which is a function of temperature and concentration of C (Fig. 5.3.9 c). In this case, C concentration distributions in Fe change with time shown in Fig.



Fig. 5.3.9. (a) Fe-C phase diagram. (b) Enlarged rectangular region in (a). (To be continued)



Fig. 5.3.9 (continued). (c) Schematic illustration of carbon distribution in iron as a function of time at 740° C. (To be continued)

5.3.9 c. The interface is in equilibrium state when it is saturated with carbon (Fe[C]), but this equilibrium is instantaneously because C diffusion in Fe away from the interface C/Fe[C] breaks the equilibrium state. This causes C to dissolve from the film into Fe[C] at the interface to achieve new saturation of Fe[C] reaching a new equilibrium at the interface again. C accumulating at the interface could results in Fe₃C (an intermediate phase between C and Fe) to form, depending on the diffusion rate of C in Fe, before the system eventually becomes a single phase of a solid solution. The probability of forming a stable low-energy nucleus of a new phase on a perfect crystal is low, simply because of the increased energy due to the formation of new surfaces. The defective surface (of the substrate) is seen to greatly enhance the nucleation rate of a new phase, as both ΔG (formation) is increased and the nucleation barrier diminished. In light of the discussion of the case described above, it is understood that the $SrFeO_3/Al_2O_3$ thin film system is not at its thermal stable state. The relative mole percentage of elements, as profiled across the film and the substrate, is shown in Fig. 5.3.9d, which can be used to describe the phase transformation by analyzing the movement of the interfaces due to elemental diffusion. The horizontal axis represents the distance along the direction perpendicular to the surface of the film; therefore, thickness of each phase (layer) across the thin film system is present. The vertical axis indicates the element concentrations of the phases. The gradient for each elemental concentration line



Fig. 5.3.9 (continued). (d) a schematic diagram showing the mole concentration distribution of each component across the thin film system.

(arbitrarily determined) in a phase suggests the potential of elemental diffusion across the film. Each vertical line in the diagram represents an interface between two adjacent phases and is arranged in the order as it appears in the film system. The points of the intersections between the vertical lines and the elemental concentration curves give the equilibrium concentrations (equilibrium solubility) between the neighboring phases; for instance, point P and Q (Fig.5.3.9d) represent the equilibrium concentrations between phase Al₂O₃ and phase SrAl_{2-x}Fe_xO₄, i.e., Al₂O₃ concentrations in phase Al₂O₃ and phase SrAl_{2-x}Fe_xO₄, i.e., Al₂O₃ concentrations in phase Al₂O₃ and phase SrAl_{2-x}Fe_xO₄, interface. Thus, phase transformation due to Al₂O₃ + SrO \rightarrow SrAl₂O₄ occurs at the Al₂O₃/SrAl_{2-x}Fe_xO₄ interface. Thus, phase transformation due to Al₂O₃ + SrO \rightarrow SrAl₂O₄ occurs at the Al₂O₃/SrAl_{2-x}Fe_xO₄ interface, resulting in crystal growth of SrAl_{2-x}Fe_xO₄ by consuming Al₂O₃, thus, the interface moves towards Al₂O₃.

5.3.10. Phase in equilibrium in the Al₂O₃/SrFeO₃ system annealed at 1000°C

In the following discussion, for simplicity, the phase Al_2O_3 , $SrAl_2O_4$ and $SrFe_{12}O_{19}$ represent the phase Al_2O_3 (including Al_2O_3 based solid solutions), $SrAl_{2-x}Fe_xO_4$ and $SrFe_{12-y}Al_yO_{19}$ correspondingly.

(a) Discussion about phase couple Al_2O_3 - $SrFe_{12}O_{19}$

There is no strong evidence to prove that these two phases are in equilibrium. It is only supportive to the statement that Al_2O_3 and $SrFe_{12}O_{19}$ are in equilibrium if $SrFe_{12}O_{19}$ is the initial phase as a result of interfacial reaction between Al_2O_3 and $SrFeO_3$. $SrFe_{12}O_{19}$ is likely to occur first at the $Al_2O_3/SrFeO_3$ interface because they both have a hexagonal structure. Some specific orientation between the phases providing similar crystal plane

structure could facilitate the new phase to nucleate due to low interface energy, therefore, formation of this phase needs lower energy to overcome the barrier due to interface creation. From this point of view this two phases are likely in equilibrium. However, the $SrFe_{12}O_{19}$ phase did not occur adjacent to Al_2O_3 at $1000^{\circ}C$, but $SrAl_2O_4$ occurred in between Al_2O_3 and $SrFe_{12}O_{19}$. This implies that $SrFe_{12}O_{19}$ is likely not the equilibrium phase to Al_2O_3 . Therefore equilibrium between Al_2O_3 and $SrFe_{12}O_{19}$ cannot be concluded at this stage.

(b) Discussion about phase couple Al_2O_3 -Sr Al_2O_4 and Sr Al_2O_4 -Sr $Fe_{12}O_{19}$: two-phase in equilibrium

In a ternary system, according to the Gibbs' phase rule, the maximum number of phases in equilibrium is four (the Gibbs' phase rule will be discussed in the latter section). Two or three phases in equilibrium also can occur depending on the condition of the system. Therefore, in the following discussion, the terms two-phase (double-phase) in equilibrium and three–phase (triple-phase) in equilibrium will be used meaning that the two or three phases involved are in equilibrium at a given condition.

Phase $SrAl_2O_4$, as an interfacial reaction product, is adjacent to Al_2O_3 at one side forming an interface $Al_2O_3/SrAl_2O_4$ and to $SrFe_{12}O_{19}$ at the other forming an interface $SrAl_2O_4/SrFe_{12}O_{19}$ indicating that two pairs of phase couples (double-phase) are in equilibrium, i.e., one phase couple $Al_2O_3 - SrAl_2O_4$, and the other $SrAl_2O_4 - SrFe_{12}O_{19}$ are in equilibrium respectively. Therefore, the elemental concentrations of the two phases in each couple are saturated at interface $Al_2O_3/SrAl_2O_4$ and $SrAl_2O_4/SrFe_{12}O_{19}$ respectively (refer Fig. 5.3.9d). The concentrations of the phases in equilibrium will be discussed later in the section "Concentrations of phases in equilibrium". Note that this two set of double-phase in equilibrium among the three phases cannot defer that the three phases are in triple-phase equilibrium. This will be discussed in the section " Gibbs' phase rule application in the Al_2O_3 /SrFeO₃ system".

(c) Discussion about the phase couple $SrAl_2O_4 - SrFeO_3$, $SrFe_{12}O_{19}$ - $SrFeO_3$ and $SrAl_2O_4 - SrFe_{12}O_{19}$: triple-phase in equilibrium

As indicated in Fig.5.3.7, $SrAl_2O_4$ and $SrFe_{12}O_{19}$ appeared in the same layer. It does not offend against Gibbs' phase rule that two phases occur within a layer in a ternary system. The fact that both phases are in contact with $SrFeO_3$ means that phase $SrAl_2O_4$ and $SrFe_{12}O_{19}$ are the equilibrium phases with $SrFeO_3$ respectively. In the meantime $SrAl_2O_4$ and $SrFe_{12}O_{19}$ are also in equilibrium as discussed in previous section. This is suggesting that there is a triple-phase in equilibrium in the system, i.e., phases $SrAl_2O_4$, $SrFe_{12}O_{19}$ and $SrFeO_3$ are in equilibrium at this thermal condition.

(d) Application of the Gibbs' phase rule to the $Al_2O_3/SrFeO_3$ system

The Gibbs' phase rule is stated simply as $\Phi = C - P + 2$, where Φ , a measure of freedom degree of a system, is the variance number of state variables that must be independently fixed or determined, C is the number of components, and P represents the number of phases observed. The factor of 2 arises from the normal number of intensive variables, temperature T and pressure P. $\Phi = C - P + 1$, when dP = 0, as is in the solid-state systems. If the Gibbs' phase rule is applied to the case of double- phase in equilibrium in a ternary system, Φ is then equal to 2, which means both temperature and elemental concentration of the phases can be changed without changing the number of phases, in other words, the two phases in equilibrium can exist in a range of temperature, and the equilibrium concentrations between these two phase can vary not only with temperature but also independently without altering the existence of the phases. For the case of triplephase equilibrium, Φ is then equal to 1. The freedom degree is one for the system, i.e., temperature. The system is only allowed to change the temperature if the number of phases remains unchanged. In terms of the case that two phases exist within a single layer in the above discussed ternary system, the system is still metastable, because Φ is 2 implying that the composition of the phases in this layer can be changed through, for example, diffusion, allowing the phases to grow even at dT = 0 (constant temperature). It should be noted that three phases are not possible to coexist within a layer in a diffusion couple of a ternary system at a constant temperature, unless it is the only homogeneous state without any neighboring layer or phases. This is because this condition gives Φ equal to 0, indicating that there is no freedom for the three phases to change their status, i.e., the three phases are in equilibrium. If so, the chemical potential μ_i of element i (i stands for any component of the system) among the phases are equal, therefore there is no driving force for the phases to evolve. This is contradictory to the fact.

5.3.11. Phase diagram of the SrO-Al₂O₃-Fe₂O₃ ternary system at 1000°C

(a) The significance of a phase diagram

A ternary phase diagram is considered to build up for the system under study. This is because for multicomponent equilibrium, the phase diagram is the basic means of
presenting physical information for a compositionally related series of systems; A phase diagram is an effective tool for demonstrating a complex reaction processes between thermodynamically compatible phases in chemically complex systems; Most oxide phase diagrams represent working hypotheses on equilibrium behavior, and are presented without significant mathematical detail through the diagram. A limited number of data points can be used to give a broad view of the equilibrium thermodynamics governing phase behavior and compatibility without recourse to mathematical description. The phase diagram describes states of equilibrium that are observed only before or after a phase transition has taken place. Based on the present data obtained from the Al₂O₃/SrFeO₃ thin film system, and in the light of the thermodynamics analysis as well as related discussions, a phase diagram of the isothermal section for the SrO-Al₂O₃-Fe₂O₃ ternary system at $T = 1000^{\circ}$ C is proposed as shown in Fig.5.3.11.

(b) Determination of the components of the phase diagram

For a multiconponent system the number of components is the same as the number of independent chemical potentials. The maximum number generally considered is the number of chemical elements. But this is often reduced by stoichiometric or structural arguments in dealing with condensed phase equilibrium. Therefore, the phase diagram is constructed by using the oxides Al_2O_3 , Fe_2O_3 and SrO as the three components, instead of Sr, Fe, Al and O, to form a ternary phase representation since the Al, Fe, Sr and O is the basic element of the compound and each metal occurs as an oxide.

(c) Determination of single phase zone

The position of a compound in a ternary system can be obtained with the equilateral "composition triangle" as shown in Fig. 5.3.11a. A single phase zone for a phase to exist in the diagram can be determined by finding the points representing its equilibrium concentrations with other phases, thus the zone is formed by connecting the points determined in the triangle. Compositions at the corners of the triangle correspond to the pure components SrO, Al₂O₃ and Fe₂O₃. Along the edges of the triangle are found compositions corresponding to the three binary subsystems SrO-Al₂O₃, Al₂O₃-Fe₂O₃ and Fe₂O₃-SrO. Lines of constant mole fraction X_{Fe2O3} are parallel to the SrO-Al₂O₃ and Al₂O₃-Fe₂O₃ edge, while lines of constant X_{Al2O3} and X_{SrO} are parallel to the SrO-Fe₂O₃ and Al₂O₃-Fe₂O₃

In the SrO-Al₂O₃ edge of the triangle, there are three phases, SrAl₂O₄, SrO and Al₂O₃. The equilibrium solubility (concentration) of SrO in Al₂O₃ is represented by a point in the SrO-Al₂O₃ edge near the corner of Al₂O₃. A point in the triangle represents a single phase when the concentration range of a phase is neglected. Ex., if equilibrium concentration of Al₂O₃ and Fe₂O₃ in SrO is neglected, the single phase zone of SrO is represented by the SrO corner in the triangle. A single phase zone in a binary system is defined by its phase equilibrium solubility with the phases in equilibrium in the binary system. Ex., equilibrium solubility of Al₂O₃ in SrAl₂O₄ and SrO in SrAl₂O₄ are represented by points b and b' beside the compound SrAl₂O₄ on the edge of Al₂O₃-SrO, respectively, as shown in Fig.5.3.11a. Therefore b-b' is the single phase zone of SrAl₂O₄ in the binary system Al₂O₃-SrO. Considering that SrAl₂O₄ is also used to denote the single phase zone in the triangle becomes critical in

determining the phase zone of $SrAl_2O_4$ since it represents the equilibrium solubility of Fe₂O₃ in SrAl₂O₄. The position of SrAl_{2-x}Fe_xO₄ must be determined in order to build a complete zone for the phase SrAl₂O₄. The position for a compound containing the three components can be determined by using the equilateral composition triangle shown in Fig.5.3.11a. To determine this position, it is helpful if $SrAl_{2-x}Fe_xO_4$ is written as [SrO (1x)Al₂O₃] xFe₂O₃, since SrAl_{2-x}Fe_xO₄ is the compound with a mole fraction ratio of $SrO/Al_2O_3/Fe_2O_3$ equal to 1/(1-x)/x. Therefore, the work to locate the position representing the compound SrAl_{2-x}Fe_xO₄ includes two steps, the first is to define the position of $[SrO (1-x)Al_2O_3]$ and the second is to determine the position representing the [SrO (1-x)Al₂O₃] xFe₂O₃. The position of [SrO (1-x)Al₂O₃] can be found on the edge of Al_2O_3 -SrO, which is the intersection of line mm' with edge Al_2O_3 -SrO dividing the edge into two parts with length ratio of SrO to Al_2O_3 equal to 1/(1-x) as pointed by an arrow (Fig. 5.3.11a). Connecting the intersection with the corner of Fe₂O₃ to form line mm', all the points on line mm' represent compounds containing a constant ratio of SrO to Al₂O₃, i.e., 1/(1-x). The position of [SrO (1-x)Al₂O₃] xFe₂O₃ is then determined by finding the point on line mm' which defines the relative mole fraction of $[Sr (1-x)Al_2O_3]$ to Fe₂O₃ equal to 1/x. This is realized by drawing the line xx' parallel to the Al₂O₃-SrO edge at point S on line mm', which divides the mm' line into two part with the length ratio of 1/x. Since all the points on line mm' represent compounds containing a constant ratio of $SrO/Al_2O_3 = 1/(1-x)$, thus, point S represents the compound $SrAl_{2-x}Fe_xO_4$ and the phase zone of SrAl₂O₄ is defined by bb'S. Since SrO is not considered to be a solid solution at this stage, this phase is represented by the corner point SrO of the triangle. As a result, phase zones in the edge SrO-Al₂O₃ of the diagram are defined, where a is denoted to the phase Al₂O₃-based solid solution, *s* to SrO, and *sa* to SrAl₂O₄ as shown in Fig.5.3.11b. The same approach is applied to the other parts of the triangle. As a result, the SrFe₁₂O₁₉ phase as a mid-phase between Sr₂Fe₂O₅ and Fe₂O₃ is set at edge SrO-Fe₂O₃ of the triangle with arbitrarily selected equilibrium concentrations with the two neighboring phases (Sr₂Fe₂O₅ and Fe₂O₅). Furthermore, compound SrFe_{12-y}Al_yO₁₉ is determined and represented by point V as shown in Fig. 5.3.11b.



Fig. 5.3.11. (a) The equilateral ternary composition triangle of components SrO, Al_2O_3 and Fe_2O_3 . (To be continued)

(d) Relating the phases in equilibrium

As discussed in the section of 5.3.10 (b) the $SrAl_{2-x}Fe_xO_4$ phase is in double-phase equilibrium with the phases Al_2O_3 and $SrFe_{12-y}Al_yO_{19}$ so that solid Alkemade lines SU

and SV are drawn to connect these two pairs of phases respectively. Since $SrFe_{12-y}Al_yO_{19}$ could be in equilibrium with Al_2O_3 , but less evident to confirm it, therefore a dashed line U'V' is used between these two phases. Note the points U and V do not represent the equilibrium concentrations between Al_2O_3 and $SrFe_{12-y}Al_yO_{19}$. In a thin film system of multi-double-phase in equilibrium, each phase has a concentration gradient within it and a distinct saturated concentration built up at the interface to the phase with which it is in equilibrium as illustrated in Fig.5.3.9d, therefore, the equilibrium concentration between



Fig.5.3.11 (continued). (b) Proposed isothermal section of the ternary phase diagram of $SrO-Al_2O_3-Fe_2O_3$ at 1000°C.

 Al_2O_3 and $SrFe_{12-y}Al_yO_{19}$ are denoted by U' and V', respectively, as shown in Fig. 5.3.11b. On the other hand, $SrAl_{2-x}Fe_xO_4$, $SrFe_{12-y}Al_yO_{19}$ and $SrFeO_{2.5}$ are in triple-phase equilibrium, unlike the case of phases in double-phase equilibrium, the equilibrium concentrations among the three phases are fixed at a given temperature. As a result, solid Alkemade lines are used to connect the points S, V and W representing the saturated concentrations of these three phases as shown in Fig.5.3.11b.

It should be noted that assumptions have been made in the construction of the isothermal section of the ternary phase diagram.

(1) Modern microscopic methods have altered the scale on which the system is viewed but have not altered the validity of Gibbs work; therefore, the thin film system can be used as diffusion system to determine thermodynamic status of phases in the system.

(2) The phases present in the diagram are based on experimental results of the $SrFeO_3$ / Al_2O_3 thin film system as a thermal diffusion couple. However, not all the phase could be able to occur in a thermal diffusion couple because some phases even are in favor of thermal dynamic condition they could be prohibited from appearing due to the kinetic condition. ^[104, 124]

(3) There was no phase transformation during the quenching of the thin film system from the annealing temperature to RT. Therefore, the phases found at RT represent the phases appeared at 1000°C.

(4) One of the advantages in determining phase diagram based on interfacial structure analysis in thermal diffusion couples using analytical TEM is that the concentrations of the phases in equilibrium can be accurately obtained at the interface. This is more advanced than x-ray especially when the phases contain multiple elements since it is impossible for x-ray diffraction to obtain quantitatively the amount of an element which is off the stoichiometric formula of a compound, although changes in lattice parameters can be examined by x-ray diffraction.

5.4. Conductometric Sensing Response

5.4.1. The Arrhenius description of conductivity of thin film SrFeO₃

By measuring the electrical conductance of thin film SrFeO₃ during exposure to various gas compositions at different temperatures, it is possible to determine relationships existing between conductivity, temperature and oxygen partial pressure. In general, the conductivity of a semiconducting metal oxide in equilibrium with oxygen at partial pressure $P_{(O_2)}$ can be described with the following equation^{187, 188}

$$\sigma = A \exp(-\frac{\varepsilon_A}{kT}) P_{O_2}^{1/N}$$
(5.4.1)

where σ is the electrical conductivity. ε_A is the apparent activation energy for conduction; A is a constant; k is the Boltzmann constant and T is the temperature in degrees Kelvin. The values typical for |1/N| are ranging from 1/6 to 1/4. The values of 1/N are positive for p-type and negative for n-type conduction. By plotting the logarithm of the equation, the activation energy, ε_A versus temperature is obtained.

5.4.2. The definition of sensitivity of sensor materials

Sensitivity is defined as change in conductivity to change in $P_{(O_2)}$. 1/N reflects the sensitivity of sensor materials because by applying the definition to Eq. (5.4.1), at

constant temperature, the following relationship is given:

$$S_{OX} = \frac{d\{\log(\sigma)\}}{d\{\log(P_{O_2})\}} = 1/N$$
(5.4.2)

In the derivation, ε_A is assumed to be invariant over the $P_{(O_2)}$ range considered. Much of the prior understanding and derivation of Eq.(5.4.1) is based on the fact that an incremental change occurs in the oxygen composition in the metal oxide and only one phase exists. For the reaction of SrFeO₃ with O₂, there is an additional complexity because changes in bulk oxygen stoichiometry, and transformation of phases, will occur provided that the process kinetics is sufficiently rapid ^[1, 189]

During the higher temperature portion of programmed temperature ramps, the composition of the SrFeO₃ thin films will be changing as a result of oxygen uptake (or loss) as determined by T, $P_{(o_2)}$ and the thermodynamics of the SrFeO_{2.5+x} + O₂ system. The equilibrium oxygen partial pressure for a given value of x increases with temperature, thus for a fixed $P_{(o_2)}$, the value x will decrease with increasing temperature. However, the kinetics of oxygen exchange between the gas phase and the SrFeO_{2.5+x} films becomes progressively slower with decreasing temperature so that for $T < 200^{\circ}$ C there is essentially no further compositional change occurring under the conditions used for this study.

5.4.3. Conductance versus Temperature: Data for the SrFeO₃ thin films deposited on the single crystal and sintered alumina substrates

The study ^[11] has showed that large variation in conductance was observed between

SrFeO_{2.5+x} in the oxygen rich CP phase, versus the oxygen deficient (BM) phase, for a typical SrFeO_{2.5+x} thin film during exposures to a series of different $P_{(O_2)}$ in O₂/N₂ mixture, which highlights one potential advantage of SrFeO_{2.5+x} for use in gas sensor applications when electrical resistance is used as a transduction signal. Over the temperature range of $300 < T < 500^{\circ}C$, the conductance difference between the CP and BM phases is greater than 2 orders of magnitude. For $T < 300^{\circ}C$ the BM form is essentially an insulator.

SrFeO_{2.5+x}/Al₂O₃ (single crystalline and sintered Al₂O₃) obtained at 700°C were evaluated for thin film conductometric sensing applications because of their good interfacial thermal stability. The conductance response of the films to temperature over the range of $300 < T < 500^{\circ}C$ is shown in Fig.5.4a as a set of Arrhenius plots. The results indicate that films deposited onto both single crystal and sintered Al₂O₃ substrates exhibited a similar temperature dependence of conductivity in air. In the high temperature region, $370 < T < 500^{\circ}C$, the relationship $\ln(\sigma)$ versus 1/T is approximately linear. The relationship then exhibits a gradual change in slope in the temperature region, $250 < T < 370^{\circ}C$ and becomes approximately linear again over the temperatures $T < 250^{\circ}C$. In this temperature region, (i.e., $370 < T < 500^{\circ}C$), both the rate of oxygen exchange between the gas and solid phase, and the rate of oxygen ion diffusion in the lattice is rapid as has been previously demonstrated in TGA and DTA measurements², and thermodynamic studies¹. This ensures that the consequent phase conversions are occurring with no kinetic arrests in this temperature and composition range. However, the conductance response to temperature is greater for the thin films deposited onto sintered Al₂O₃ than single crystal Al₂O₃ as show in Fig. 5.4a. One of the possible reasons causing this difference is due to the difference in thickness between the films of the two systems. Conductivity is defined as $G = 1/\rho$, where ρ is electrical resistivity. $\rho = R \frac{A}{L}$, where R (measured in ohms, Ω) is the electrical resistance of a uniform specimen of the material; L, (measured in metres, m), is the length of the specimen; A, (measured in square metres, m²), is the cross-sectional area of the specimen. In a regular three-dimensional conductor, the resistance can be written as

$$R = \rho \frac{L}{A} = \rho \frac{L}{Wt} = \frac{\rho}{t} \frac{L}{W} = R_s \frac{L}{W},$$

where W is the sheet width and t is the thickness. R_s is named Sheet Resistance because it multiplied by a dimensionless quantity, the units are ohms. The term Sheet Resistance is used for a measure of resistance of thin films that have a uniform thickness with a unit of ohms/square (Ω/\Box). For a square, L = W, then $R = R_s$ for any size square. Since the conductivity is measured with the two pole method, the conductivity

$$G_c = \frac{1}{\rho} = \frac{t}{\rho t} = \frac{1}{R_s t} = \frac{I}{Vt},$$

where I is the measured electrical current and V is the voltage applied to the poles of the circuit. This equation implies that conductivity G_c is equal to the amount of the current I per unit thickness of the film under a fixed voltage. I increases with increase of thickness, t, of the film. i.e., I will be measured to be higher if the film is thicker. On the other hand, if the film thicknesses in the two thin film systems are considered the same, in the other words, if the same value of thickness, t, is used to calculate the G_c for the two

systems, since G_c will be represented by the value of *I*, the one which is actually thicker will yield a greater value of G_c (because of higher value of *I*) than the other. In fact, the film on the sintered Al₂O₃ is thicker (60nm), as measured on the image of the cross section specimen, than the film (38nm) on the single crystal Al₂O₃, but the same thickness is considered due to the same deposition conditions, therefore, the same *t* is used in the program to calculate G_c for the films of the two systems resulting in high value of G_c for the thin film system with sintered Al₂O₃.



Fig. 5.4. (a) Arrhenius plots for the films $SrFeO_{2.5+x}$ on single crystalline and sintered polycrystalline Al_2O_3 in air. (To be continued)



Fig. 5.4 (continued). (b) Resistance response at 500° C of the SrFeO_{2.5+x} films on the single crystalline and sintered Al_2O_3 substrates to oxygen and (c) to propane.

60

80

propane

40 **Time / minutes**

(c)

20

0

The other factors affecting the G_c value include crystal defects such as grain boundaries, and cavities at joints of the grains in the film or on the surface of the sintered Al₂O₃, which could play a noticeable role in reducing the conductivity of the film because these defects act like breaking the continuity of the film, therefore increase the electrical resistance.

Fig. 5.4b and c show the resistance response of the $SrFeO_3$ films on the two different substrates to exposure to oxygen (6%) and propane in background air at 500°C respectively. Both the oxygen and propane *p*-type gas sensor responses at 500°C were similar, although the response to propane was not as reversible with the film deposited onto the single crystal Al_2O_3 substrate. Nevertheless, the films can be used to detect reducing gases by monitoring the change in film resistance with gas exposure at this temperature with assurance of excellent thermal stable behavior of the thin films system.

5.5. Conclusions to the SrFeO₃/Al₂O₃ thin film system

The $SrFeO_3/Al_2O_3$ thin film systems (single crystalline and sintered Al_2O_3 substrates) grown by PLD at different temperatures with additional post-deposition thermal treatments have been characterized using TEM for the thin film system structures and interfacial reactions.

The SrFeO₃ film deposited at room temperature demonstrated poor adhesion to the Al_2O_3 substrate. Adhesion is improved in the system deposited at higher temperatures.

Interfacial reactions initiated in the SrFeO₃/Al₂O₃ thin film system ($T_{dep} = 700^{\circ}$ C, 20min) after annealing at 700°C for 10 hours followed by an additional annealing at 850°C for 5 hours.

Phase transformation and reactions at the interface of the thin film system was identified on the sample after annealing at 700°C for 10 hours and 1000°C for 5 hours. The phases formed at the interface of $SrFeO_3/Al_2O_3$ were characterized to be $SrAl_{2-x}Fe_xO_4$ and $SrFe_{12-y}Al_yO_{19}$.

A ternary reduced-phase diagram SrO-Al₂O₃-Fe₂O₃ at the isothermal section of 1000°C is proposed based on the interfacial structure and the phase transformation occurred in the SrFeO₃ thin film system at temperature T = 1000°C.

Both systems (SrFeO₃ with single crystal and sintered Al_2O_3 substrates) possess high interfacial stability and show similar sensor response to oxygen and propane at 500°C, and can be taken as comparable sensor systems to detect reducing gases at this temperature with assurance of excellent thermal stable behavior of the thin films system.

Chapter 6

Summary and conclusions

A review of basic crystal structures, fundamental properties, applications and characterizations of perovskite SrFeO₃ and related materials has been presented. Kinetic phenomena in thin film systems, such as diffusion, interfacial reactions, amorphization are introduced. Principles of advanced experimental methods relating characterization of thin films, such as microscopy and electron diffraction, are discussed.

The study on the thermal stability of the SrFeO₃/SiO₂/Si and SrFeO₃/Al₂O₃ systems was conducted using analytical transmission electron microscopy.

In the SrFeO₃/SiO₂/Si system, the SrFeO₃ film deposited at RT consists of a layer of nano-sized crystallites and a layer of amorphous domains adjacent to the SiO₂/Si substrate. The amorphous contains the same elemental composition as the crystallites Formation of the amorphous phase of the film is due to the effect of the amorphous substrate SiO₂.

High resolution imaging of TEM showed to be a more effective method than x-ray diffraction in distinguishing nano-crystalline structure from amorphous.

In the SrFeO₃/SiO₂/Si system grown at 450°C for 4 minutes, the SrFeO₃ film possesses the same structure as the film deposited at RT, but the relative amount of crystallites to

the amorphous is much smaller due to amorphous growth. The crystallites at the outermost surface of the thin film system deposited at 700°C for 4 minutes possesses preferential orientations [111] and [112] perpendicular to the surface, and the layered amorphous phase contains Sr, Fe, O with additional Si. Annealing at 700°C for 1 hour results in the crystalline SrFeO₃ layer transforming to a hexagonal phase Sr(Fe,Si)₁₂O₁₉. Longer period annealing results in an increased growth of the previously identified crystalline phase Sr(Fe,Si)₁₂O₁₉ and precipitation of nano-sized crystalline grains SrO_X within the amorphous region of the film.

The existence of SiO_2 , as a buffer layer on the silicon substrate, promotes the formation of amorphous phases in the film at the $SrFeO_3/SiO_2$ interface and is the source of thermal diffusion of silicon into the perovskite thin film. Therefore, SiO_2 is not a suitable choice of material for a diffusion barrier to construct stable $SrFeO_3$ thin film gas sensors which require operation at elevated temperatures.

The study on the SrFeO₃/Al₂O₃ (single crystalline and sintered Al₂O₃ substrates) thin film systems showed that interfacial reactions initiated in the thin film system SrFeO₃/Al₂O₃ ($T_{dep} = 700^{\circ}$ C, 20min) after additional annealing at 700°C for 10 hours and 850°C for 5 hours, suggesting excellent thermal stability of the system. Phase transformation and reactions occurred at the interface of the SrFeO₃/Al₂O₃ thin film system after annealing at 700°C for 10 hours followed by annealing at 1000°C for 5 hours. The phases formed at interface SrFeO₃/Al₂O₃ were characterized to be SrAl_{2-x}Fe_xO₄ and SrFe_{12-y}Al_yO₁₉. Thermal equilibrium relationship of phases in the $SrFeO_3/Al_2O_3$ system is discussed based on the interfacial structure and the phase transformation occurred in the $SrFeO_3$ thin film system at temperature $T=1000^\circ C$. As a result, the isothermal section at $1000^\circ C$ of the ternary phase diagram $SrO-Al_2O_3$ -Fe₂O₃ is proposed with phases identified, phase regions and relationship of phase in equilibrium.

Test on the conductometric sensing response of the system indicates that both systems $(SrFeO_3 \text{ with single crystal and sintered } Al_2O_3 \text{ substrates})$ possess similar conductometric (electrical) properties, i.e., a sensor response to oxygen and propane at 500^oC, and can be taken as comparable sensor systems to detect reducing gases at this temperature with assurance of excellent thermal stable behavior of the thin films system.

Chapter 7

Original contribution to knowledge

7.1. High resolution TEM imaging is an advanced characterization method in determination of crystalline and amorphous of nano-structured materials

This work permitted the high resolution imaging on the characterization of thin film system SrFeO₃/SiO₂/Si. The study has proved that TEM high resolution imaging is the effective way to characterize crystallography of nano-structured thin film materials (not limited to it). It provided solid evidence that nano-crystalline materials and amorphous materials can be revealed at atomic scale, therefore they can be distinguished from each other, unlike x-ray diffraction, the distinguishable characters between nano-crystalline and amorphous do not exist in the x-ray spectra due to the effects of grain size and crystal defects on x-ray diffraction. Since x-ray diffraction cannot provide determinable information between nano-crystalline and amorphous, an amorphous could be wrongly confirmed as crystalline or vice versa. HRTEM imaging has shown its advantage over the X-ray diffraction in thin film characterization by providing direct view of lattice images for crystalline materials, which is exclusive in determining crystal structure.

7.2. Thermal stability is significant factor in assuring functionality of thin film sensing applications

The study on the SrFeO₃/SiO₂/Si system found that silicon diffusion and reaction with the SrFeO₃ film occurred during deposition at 700°C for 4 minutes, resulting in amorphous morphology of the film. Phase transformation of the crystalline SrFeO₃ to a hexagonal

phase $Sr(Fe,Si)_{12}O_{19}$ was observed after longer period annealing at 700°C. Crystallization within the amorphous region of the film was fund to form crystalline grains SrO_X . The existence of SiO₂ promoted the formation of amorphous phases in the film at the $SrFeO_3/SiO_2$ interface and was the source of thermal diffusion of silicon into the perovskite thin film. Therefore, it is concluded that SiO₂ is not a suitable choice of material for a diffusion barrier to construct stable $SrFeO_3$ thin film gas sensors for silicon based structures which require operation at elevated temperatures.

The TEM study of thermal stability of the SrFeO₃/Al₂O₃ system shows that interfacial reactions initiated in the thin film system deposited at 700°C for 20min after additional annealing at 700°C for 10 hours and 850°C for 5 hours. It is obvious that substrate plays an important role in thermal stability of thin film devices and suggesting that Al₂O₃ is the relatively thermal stable substrate materials for device performing at elevated temperatures. This also suggests that Al₂O₃ in thin film devices for a better cost efficiency in device manufacturing. SrFeO₃ with single crystal and sintered Al₂O₃ substrates possess high interfacial stability and show similar conductometric (electrical) properties, i.e., a sensor response to oxygen and propane at 500°C, and can be taken as comparable sensor systems to detect reducing gases at this temperature with assurance of excellent thermal stable behavior of the thin films system.

7.3. Crystallographic structures of the new phases are identified in the SrFeO₃/SiO₂/Si and SrFeO₃/Al₂O₃ thin film systems

The study shows that in the as–deposited $SrFeO_3/SiO_2/Si$ thin film system at 700 °C for 4 minutes, the crystalline grains of $SrFeO_3$ possess preferential orientations [111] and [112] perpendicular to the surface and transform to a hexagonal phase $Sr(Fe,Si)_{12}O_{19}$ after longer period annealing at 700°C. The formation of the amorphous phase of the film and the amorphous morphology are affected by the SiO₂ amorphous substrate. Nano-sized crystalline grains SrO_x precipitated in the amorphous phase are identified, which signifies initial crystallization of the amorphous phase in the film.

In the $SrFeO_3/Al_2O_3$ system, initial phase transformation and reactions at the interface at $850^{00}C$ are identified. Crystallographic structures of the new phases, as the products of the interfacial reactions between $SrFeO_3$ and substrate Al_2O_3 at $1000^{0}C$, are characterized to be $SrAl_{2-x}Fe_xO_4$ and $SrFe_{12-y}Al_yO_{19}$.

In light of the phase identification, an isothermal section at 1000° C of the ternary phase diagram SrO-Al₂O₃-Fe₂O₃ is proposed in which information regarding phases; phase regions and their thermal equilibrium relationship are present.

Chapter 8

Suggested future studies

According to the success on the characterization of the $SrFeO_3/SiO_2/Si$ and $SrFeO_3/Al_2O_3$ thin film systems, suggestions for the future work can be given:

(1) Economically, since Al_2O_3 exhibits excellent thermal stability, it can be taken as a thermal barrier to replace the expensive single crystalline Al_2O_3 in the perovskite sensing devices in order to achieve better cost-efficiency in device manufacturing. However, the study of the thermal stability of the Al_2O_3 thin film barrier or different combination of multi-thin film barriers is needed for individual thin film system.

(2) Scientifically, in order to quantitatively construct the isothermal section at 1000° C of the SrO-Al₂O₃-Fe₂O₃ ternary phase diagram, the solid solutions of the components SrO, Al₂O₃ and Fe₂O₃, as well as the SrAl_{2-x}Fe_xO₄ and SrFe_{12-y}Al_yO₁₉ phases have to be quantitatively determined.

References

- 1 M.L. Post, B.W. Sanders, and P. Kennepohl: Thin Films of Non-Stoichiometric Perovskites as Potential Oxygen Sensors. *Sensors and Actuators* B 13-14, 272 (1993).
- 2 Y. Takeda, K. Kanno, T. Takada, O. Yamamoto, M. Takano, N. Nakayama, and Y. Bando: Phase Relation in the Oxygen Nonstoichiometric System, $SrFeO_x$ ($2.5 \le x \le 3.0$). J. Solid State Chem. 63, 237 (1986).
- 3 S. Wissman, and K.D. Becker: Localization of Electrons in Nonstoichiometric SrFeO₃-Delta. *Solid State Ionics*, *85*, 279 (1996).
- 4 J. Hombo, Y. Matsumoto, and T. Kawano: Electrical conductivities of $SrFeO_{3-\delta}$ and $BaFeO_{3-\delta}$ perovskites. *Journal of Solid State Chemistry*, 84, 138 (1990).
- 5 K. Ichimura, Y. Inoue, I. Yasumori: Hydrogenation and Hydrogenalysis of Hydrocarbons on Perovskite Oxides; B. Viswanathan: Co Oxidation and NO Reduction on Perovskite Oxides; T. Arakawa, Perovskite Oxides as Solid State Chemical Sensors, in Properties and Applications of Perovskite-Type Oxides, edited by L.G. Tejuca and J.L.G. Fierro (Marcel Dekker, New York, 1993), pp..235, 271, 361.
- 6 D.E. Williams: Conduction and Gas Response of Semiconductor Gas Sensors, in Solid State Gas Sensors, edited by P.T. Moseley and B.C. Tofield (The Adam Hilger Series on Sensors, Bristol and Philadelphia, 1987), Chapt.5.
- 7 G. Eranna, B.C. Joshi, D.P. Runthala, and R.P. Gupta: Oxide Materials for Development of Integrated Gas Sensors – A Comprehensive Review. Critical Reviews in *Solid State and Materials Sciences* 29, 111 (2004).
- 8 M.L. Post, J.J. Tunney, D. Yang, X. Du, and D.L. Singleton: Material Chemistry of Perovskite Compounds as Chemical Sensors. *Sensors and Actuators* B 59, 190 (1999).
- 9 J.J. Tunney, M.L. Post, X. Du, and D. Yang: Temperature Dependence and Gas-Sensing Response of Conduction for Mixed Conducting SrFe_yCo_zO_x Thin Films. *Journal of the Electrochemical Society* 149 (6), H113 (2002).
- 10 G. Martinelli, M.C. Carotta, M. Ferroni, Y. Sadaoka, and E. Traversa: Screen Printed Perovskite-Type Thick Films as Gas Sensors for Environmental Monitoring. *Sensors and Actuators* B 55, 99 (1999).
- 11 J.J. Tunney and M. L. Post: The Electrical Conductance of SrFeO_{2.5+x} Thin Films. *Journal of Electroceramics* 5:1, 63 (2000).

- 12 K. Sahner, R. Moos, M. Matam, J.J. Tunney, and M.L. Post: Hydrocarbon Sensing with Thick and Thin Film p-type Conducting Perovskite Materials. Sensors and Actuators B 108, 102 (2005).
- 13 N. Barsan and U. Weimar: Conduction Model of Metal Oxide Gas Sensors. J. of Electroceramics 7, 143 (2001).
- 14 C. Xu, J. Tamaki, N. Miura, and N. Yamazoe: Grain Size Effects on Gas Sensitivity of Porous SnO₂-Based Elements. *Sensors and Actuators* B 3, 147 (1991).
- 15 D.E. Williams and K.F.E. Pratt: Microstructure Effects on the Response of Gas-Sensitive Resistors Based on Semiconducting Oxides. *Sensors and Actuators* B 70, 214 (2000).
- 16 Z. Wang, T. Sasaki, N. Koshizaki, J.J. Tunney, and M.L. Post: Crystallized SeFeO_{3-x} Films Deposited by Pulsed Laser Deposition without in-situ Substrate Heating. *Thin Solid Films* 437, 95 (2003).
- 17 B.R. Sanders, J. Yao, and M.L. Post: Thin Films of SrFeO_{2.5+x} Effect of Preferred Orientation on Oxygen Uptake, in Polycrystalline Thin Films: Structure, Texture, Properties and Applications, edited by, K. Barmak, M.A. Parker, J.A. Floro, R. Sinclair, and D.A. Smith (*Materials Research Society* Symposium Proceedings 343, San Francisco, U.S.A 1994), p.463.
- 18 J.J. Tunney, P. Whitfield, X. Du, and M.L. Post: Pulsed Laser Deposition, Characterization and Thermochemical Stability of SrFe_yCo_{1-y}O_x Thin Films. *Thin Solid Films* 42, 221 (2003).
- 19 R. Moos, F. Rettig, A. Hürland, and C. Plog: Temperature- Independent Resistive Oxygen Exhaust Gas Sensor for Lean-Burn Engines in Thick-Film Technology. *Sensors and Actuators* B 93, 43 (2003).
- 20 S.J. Litzelman, A. Rothschild, and H.L. Tuller: The Electrical Properties and Stability of $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ Thin Films for Automotive Oxygen Sensor Applications. Sensors and Actuators B 108, 231 (2005).
- 21 X.F. Chen, H. Lu, W.G. Zhu, and O.K. Tan: Enhanced Field Emission of Silicon Tips Coated With Sol-Gel-Derived (Ba_{0.65}Sr_{0.35}) TiO₃ Thin Film. Surface and Coatings Technology 198, 266 (2005).
- 22 S.H. Oh and C.-G. Park: Nanoscale Characterization of Interfacial Reactions in SrRuO₃ Thin Film on Si Substrate. *Surface and Interface Analysis* 31, 796 (2001).
- 23 X.B. Lu, X. Zhang, R. Huang, H.B. Lu, Z.H. Chen, W.F. Xiang, M. He, B.L. Cheng, H.W. Zhou, X.P. Wang, C.Z. Wang, and B.Y. Nguyen: Thermal

Stability of LaAlO₃/Si Deposited by Laser Molecular-Beam Epitaxy. Appl. Phys. Lett. 84, 2620 (2004).

- 24 X.B. Lu, Z.G. Liu, G.H. Shi, H.Q. Ling, H.W. Zhou, X.P. Wang, and B.Y. Nguyen: Interfacial Structures of LaAlO₃ Films on Si(100) Substrates. *Applied Physics A: Materials Science & Processing* 78, 921 (2004).
- J.Q. He, C.L. Jia, V. Vaithyanathan, D.G. Schlom, J. Schubert, A. Gerber, H.H. Kohlstedt, and R.H. Wang: Interfacial Reaction in the Growth of Epitaxial SrTiO₃ Thin Films on (001) Si Substrates. J. Appl. Phys. 97, 104921 (2005).
- 26 F.S. Gallasso, Structure, Properties and Preparation of Perovskite Type Compounds, *Pergamon Press*, Oxford, 1969
- 27 J.B. Goodenough and J.M. Longo, Landolt-Börnstein Tabellen, New Series, III/4a. Springer-Verlag, Berlin, 1970
- 28 S. Nomura, Landolt-Börnstein Tabellen, New Series, III/4a. Springer-Verlag, Berlin, 1970
- 29 J.K. Burdett, G.J. Miller, J.W. Richardson Jr, J.V. Smith: Low-Temperature Neutron Powder Diffraction Study of CrO₂ and the Validity of the Jahn-Teller Viewpoint. J. Am. Chem. Soc., 110, 8064 (1988).
- 30 C.N.R. Rao and J. Gopalakrishnan, *New Directions in Solid State Chemistry*, Cambridge University Press, Cambridge, 1997, Second Edition.
- 31 C.N.R. Rao and B. Raveau, in *Transition Metal Oxides*, second edition, part I p43, Wiley-Vch New York-Chichester-Weinheim-Brisbane-Singapore-Toronto, 1998.
- 32 M.B. Robin and P. Day: Mixed valence chemistry-a survey and classification, Adv. Inorg. Chem. Radiochem., 10, 247 (1967); also see P. Day, Int. Rev. Phys. Chem. 1, 149 (1981).
- 33 C.N.R. Rao, O. Parkash, D. Bahadur, P. Ganguly, and S. Nagabhushana: Itinerant electron ferromagnetism in Sr^{2+} Ca^{2+} , and Ba^{2+} -doped rare-earth orthocobaltites $(Ln^{3+}_{1-x}M^{2+}_{x}CoO_{3})$. J. Solid State Chem., 22, 353 (1977).
- 34 S. Ueno, J. Meng, N. Kamegashira, H. Saito-Nakano and K. Enami: Crystal structure of a layered perovskite, barium europium manganese oxide BaEu₂Mn₂O₇. *Materials Research Bulletin*. Vol, 31, No5, pp 497-502 (1996).
- J.L. Fourquet, H. Duroy, and M.P. Crosnier-Lopez: Structural and Microstructural Studies of the Series Ln _{2/3-x}Li_{3x}TiO₃, J. Solid State Chem. 127, 283-194 (1996).

- 36 G. Van Tendeloo, H. W. Zandbergen, T. Okabe and S. Amelinckx: Heavy atom disorder in the high T_c superconductor $Ba_2YCu_3O_{7-\delta}$ studied by means of electron microscopy and electron diffraction. *Solid State Commun.* 63, 969 (1987).
- 37 G Van Tendeloo, H.W. Zandbergen, S. Amelinckx: The vacancy order disorder transition in Ba₂YCu₃O_{7- δ} observed by means of electron diffraction and electron microscopy, *Solid State Commun.* 63, 603 (1987)
- 38 H.W. Zandbergen, R. Gronsky, G. Thomas: Surface decomposition of superconducting YBa ₂Cu₃/O₇, *Phys. Status Solidi A 105*, 207(1988).
- 39 M. Hervieu, B. Domenges, B. Raveau, M. Post, W.R. McKinnon, J. M. Tarascon: Order-disorder phenomena in the '60 K superconductor' $YBa_2Cu_3O_{7-\delta}$ (0.37< δ) *Mater. Lett.* 8, 73(1989).
- 40 A. Hussain, L. Kihlborg: Crystal Physics, Diffraction, Theoretical and General Crystallography, *Actacrystallogr. A.32*, 551 (1976).
- 41 A. Ramanan, J. Gopalakrishnan, M. K. Uppal, D. A. Jefferson, C. N. R. Rao:Bismuth-Tungsten Oxide Bronzes: A Study of Intergrowth Phases and Related Aspects. *Proc. R. Soc. London A* 395, 127 (1984).
- 42 D.A. Jefferson, M.K. Uppal, D.J. Smith: Oxidation of bismuth-tungsten bronzes. J. Solid State Chem. 53, 101(1984).
- 43 J.L. Hutchison, A.J. Jacobson: Electron microscopy of the perovskite polytypes Ba₄Ta₃LiO₁₂ and Ba₅W₃Li₂O₁₅. Acta Crystallogr. B31, 1442 (1975).
- 44 J.L. Hutchison, A.J. Jacobson: Electron microscopy of the perovskite-related phases 4H Ba_{0.1}Sr_{0.9}MnO_{2.96},5H Ba₅Nb₄O₁₅ and 6H BaFeO_{2.79}. J. Solid State Chem. 20, 417 (1977).
- 45 V.Caignaert, M. Hervieu, B. Domenges, N. Nguyen, J. Pannetier, B. Raveau: BaMn_{1-x}Fe_xO_{3-δ}, an oxygen-deficient 6H' oxide: Electron microscopy, powder neutron diffraction, and Mössbauer study. J. Solid State Chem. 73, 107 (1988).
- 46 A. Maignan, C. Michel, M. Hervieu, C. Martin, D. Groult, B. Raveau: Tl₂Ba₂CaCu₂O₈: structure and superconductivity. *Mod. Phys. Lett. B2*, 681 (1988).
- 47 C.N.R. Rao and G.V.Subba: Electrical conduction in metal oxides. *Phys. Status Solidi, A1*, 597(1970).
- 48 J.B. Goodenough, in *Solid State Chemistry* (C.N.R. Rao, ed.), Dekker, New York, 1974.

- 49 C.N.R. Rao and G.V. Subba Rao, *Transition Metal Oxides, NSRDS-NBS Monograph 49*, U.S. National Bureau of Standards, Washington, DC, 1974.
- 50 C.N.R. Rao and J. Gopalakrishnan, *New Directions in Solid State Chemistry*, Cambridge University Press, Cambridge, 1997, Second Edition.
- 51 N. Nakayama, M. Takano, S. Inamura, N. Nakamishi and K. Kosuge: Electron microscopy study of the cubic perovskite phase SrFe $_{1-x}V_xO_{2.5+x}$, J. Solid State Chem. 71, 403-417(1987).
- 52 C.N.R. Rao. "Transition Metal Oxides" Annu. Rev. Phys. Chem., 40, 291 (1989).
- 53 A.K. Cheetham and P. Day (ed.), *Solid State Chemistry*, Clarendon Perss, Oxford, 1987.
- 54 T. Arakawa, Perovskite Oxides as Solid State Chemical Sensors, in *Properties* and Applications of Perovskite-Type Oxides, edited by L.G. Tejuca and J.L.G. Fierro (Marcel Dekker, New York, 1993), p. 361.
- 55 J.R. Stetter: A Surface Chemical View of Gas Detection, J. Colloid Interface Sci., 65: 432-443(1978).
- 56 T. Arakawa. H. Kurachi, and J. Shiokawa: Physicochemical properties of rare earth perovskite oxides used as gas sensor material. *J. Mat. Sci.*, 20: 1207-1210 (1985).
- 57 A. Nemudry, M. Weiss, I. Gainutdinov, V. Boldyrev, and R. Schöllhorn: Room Temperature Electrochemical Redox Reactions of the Defect Perovskite SrFeO2.5+x, *Chem. Mater.*10, 2403 (1998).
- 58 C. Carotta, G. Martinelli, Y. Sadaoka and P. Nunziante: Gas-sensitive electrical properties of perovskite-type SmFeO3 thick films, *Sensors and Actuators* B 48 270 (1998).
- 59 J. Gerblinger and H. Meixner, in *Sci. Technol. Electroceramic Thin Films*, O. Auciello, R. Waser (Eds), 439 (1995).
- T. Nakamura, G. Petzow, L. J. Gauckler: Stability of the perovskite phase LaBO₃ (B = V, Cr, Mn, Fe, Co, Ni) in reducing atmosphere. *Mat. Res. Bull.* 14, 649-659 (1979)
- 61 S. Katz, J.J. Croat, J.V. Laukonis: Lanthanum Lead Manganite Catalyst for Carbon Monoxide and Propylene Oxidation. *Ind. Eng. Chem. Prod. Res.* Dev. 14, 274 (1975);
- 62 D.W. Johnson, Jr., P.K. Gallagher, E.M. Vogel, F. Schrey: in *Thermal Analysis*,

I. Buzar, Ed. (Heyden, London, 1975). P.181

- 63. Y.-F Yu Yao, The oxidation of hydrocarbons and CO over metal oxides IV. Perovskite-type oxides , J. Catal. 36, 266(1975).
- 64 R.D. Shannon and C.T. Prewitt, *Acta Crystallogr*. Sect.B25, 925 (1969); ibid. 26, 1046 (1970).
- 65 Koho Yang, Jung-Hsiung Shen, Kai-Yun Yang, I-Ming Hung, Kuan-Zong Fung and Moo-Chin Wang: Characterization of the yttria-stabilized zirconia thin film electrophoretic deposited on $La_{0.8}Sr_{0.2}MnO_3$ substrate, *Journal of Alloys and Compounds*, Vol. 436, 2 14, 351 (2007).
- 66 Nguyen Q. Minh, Ceramic Fuel Cells, Journal of the American Ceramic Society Vol 76, 563-588, 1993
- 67 T. Ishihara, K. Shimose, T. Kudo, H. Nishiguchi, T. Akbay and Y. Takita, Preparation of yttria-stabilized zirconia thin films on strontium-doped LaMnO₃ cathode substrates via electrophoretic deposition for solid oxide fuel cells J. Am. Ceram. Soc. 83, 1921(2000).
- 68 J.S. Hong, K. Metha and A.V. Virkar: Effect of Microstructure and Composition on Ionic Conductivity of Rare-Earth Oxide-Doped Ceria, J. Electrochem. Soc. 145 (1998), p. 638.
- 69 I. J. M. M. Raaijmakers, A. H. Reader, and P. H. Oosting: The formation of an amorphous silicide by thermal reaction of sputter-deposited Ti and Si layers, *J. Appl. Phys.* 63, 2790(1988).
- 70 K. Holloway and R. Sinclair, Mechanically driven solid state amorphizing transformation-High-resolution and in situ tem studies of annealing of Ti-Si multilayers. *Journal of the Less Common Metals*, 140, (1988) 139.
- 71 R. Sinclair, K. Holloway, K. B. Kim, D. H. Ko, A. S. Bhansali, A. F. Schwartzman, and S. Ogawa: Phase reactions at semiconductor metallization interface. *Inst. Phys. Conf.* Ser. No.100, 599 (1989).
- 72 W. Lur and L. J. Chen: Growth kinetics of amorphous interlayer formed by interdiffusion of polycrystalline Ti thin-film and single-crystal silicon. *Appl. Phys. Lett.* 54, 1217 (1989).
- 73 Karen Holloway, Robert Sinclair, and Menachem Nathan, "Amorphous silicide formation by thermal reaction: A comparison of several metal-silicon systems. J. Vac. Sci. Technol. A7, 1479 (1989).
- 74 E. Ma, W. J. Meng, W. L. Johnson, and M.-A. Nicolet: Simultaneous Planar

Growth of Amorphous and Crystalline Silicides During Interdiffusion Reaction of Ni with Amorphous Si, *Appl. Phys. Lett.*, 53, 2033 (1988).

- 75 D. Wang and D. G. Ivey: Interfacial Reactions between Ti Thin Films and InP, Materials Science and Engineering B-Solid State Materials for Advanced Technology, V41, 289 (1996).
- D. G. Ivey and D. Wang: Low Temperature Reactions between Nickel Thin Films and InP, in *Experimental Methods of Phase Diagram Determination*, Edited By J. E. Morral, R. S. Schiffman & S. M. Merchant. Warrendale PA: TMS (1994) p151.
- 77 D. Wang, J.J. Tunney, X. Du, M.L. Post and R. Gauvin, TEM Investigation of Interfacial Reactions between SrFeO₃ Thin Films and Silicon Substrates, *J. Materials Research*, Vol.22, 76 (2007).
- 78 W.L. Johnson: Thermodynamic and kinetic aspects of the crystal to glass transformation in metallic materials. *Prog. in Mater. Sci.* 30, 81 (1986).
- 79 B.M. Clemens and R. Sinclair: Metastable phase formation in thin films and multilayers. *MRS Bull* No.2, 19 (1990).
- 80 R.B. Schwarz and W.L. Johnson, Formation of an Amorphous Alloy by Solid-State Reaction of the Pure Polycrystalline Metals. *Phys. Rew. Lett.* 51, 415 (1983).
- 81 R.W. Bené: A kinetic model for solid-state silicide nucleation. J. Appl. Phys. 61, 1826(1987).
- 82 W.Y. Hsieh, J.H. Lin and L.J. Chen: Simultaneous occurrence of multiphases in the interfacial reactions of ultrahigh vacuum deposited Hf and Cr thin films on (111)Si. *Appl. Phys. Lett.* 62, 1088 (1993).
- 83 M. Nathan: Solid phase reactions in free-standing layered M-Si (M=Ti, V, Cr, Co) films. J. Appl. Phys. 63, 5534(1988).
- ⁸⁴ J.Y. Cheng and L.J. Chen: Formation of amorphous interlayers by a solid-state diffusion in Zr and Hf thin films on silicon. *Appl. Phys. Lett.* 56, 457(1990).
- 85 V. Demuth, H.P. Strunk, D. Wörle, C. Kumpf, E. Burkel, M. Schulz: Formation of amorphous layers by solid-state reaction from thin Ir films on Si(100). J. Appl. Phys. 68, 451(1999).
- 86 M.O. Aboclfotoh, A. Alessandrini and F.M. d'Heurle: Transmission electron microscope study of the initial stage of formation of Pd₂Si and Pt₂Si. *Appl. Phys. Lett.* 49, 1242 (1986).

- 87 J.M.M. De Nijs and A. Van Silfhout: The Ti/c-Si solid state reaction: II. Additional measurements by means of RBS, XPS and AES. *Appl. Surf. Sci.* 40, 349 (1990).
- 88 J. M. M. de Nijs and A. van Silfhout: The Ti/c-Si solid state reaction: III. The low-temperature reaction kinetics. *Appl. Surf. Sci.* 40, 359 (1990).
- 89 I.J.M.M. Raaijmakers, and Ki-Bum Kim: A comparison of the reaction of titanium with amorphous and monocrystalline silicon. J. Appl. Phys. 67, 6255 (1990).
- 90 K. Holloway and R. Sinclair, Interfacial Reactions in Titanium-Silicon Multilayers. *Mat. Res. Soc. Symp. Proc.* Vol.77, 357 (1987).
- 91 I.J.M.M. Raaijmakers, A.H. Reader, and P.H. Oosting: The formation of an amorphous silicide by thermal reaction of sputter-deposited Ti and Si layers. J. *Appl. Phys.* 63. 2790 (1988).
- 92 J.Y. Cheng and L.J. Chen: Formation of amorphous interlayers by solid-state diffusion in ultrahigh-vacuum-deposited polycrystalline Nb and Ta thin films on (111)Si. *Appl. Phys. Lett.* 58, 45 (1991).
- 93 J.Y. Cheng and L. J. Chen: Growth kinetics of amorphous interlayers by solidstate diffusion in ultrahigh vacuum deposited polycrystalline Nb and Ta thin films on (111)Si. J. Appl. Phys. 69, 2161 (1991).
- 94 J.R. Abelson, K.B. Kim, D.E. Mercer, C.R. Helms, R. Sinclair, and T.W. Sigmon, J. Appl. Phys, 63, 689 (1988.)
- 95 R. Anton and U. Neukirch: Comparative AES and RHEED study of the formation of Pd silicide on clean and oxide covered Si(100) and (111) surfaces. *Appl. Surf. Sci.* 29, 287 (1987).
- 96 K. Konuma, J. Vrijmoeth, P.M. Zagwijn, J.W.M. Frenken, E. Vlieg. and J.F. van der Veen: Formation of epitaxial β -FeSi2 films on Si(001) as studied by medium-energy ion scattering. *J. Appl. Phys.* 73, 1104 (1993).
- 97 J. Alvarez, J.J. Hinarejos, E.G. Michel and R. Miranda: Study of the electronic structure of iron silicides grown on $Si(100)2 \times 1$ by reactive deposition epitaxy. *Surf. Sci.* 269/270, 1011 (1992).
- J. F. Van der Veen, A.E.M.J. Fischer, and J. Vrijmoeth: Nickel and cobalt silicides on silicon: Thin-film reaction and interface structure. *Appl Surf. Scci.* 38, 13 (1989).

- R.T. Tung: Epitaxial CoSi₂ and NiSi₂ thin films. *Mater. Chem. Phys.* 32, 107 (1992).
- 100 J. Y. Veuillen J. Derrien, P.A. Badoz, E. Rosencher, and C. d'Anterroches: Co/Si(111) interface: Formation of an initial CoSi₂ phase at room temperature. *Appl Phys. Lett.* 51, 1448 (1987).
- 101 R.W. Balluffi, and J.M. Blakely: Special aspects of diffusion in thin films. *Thin Solid Films* 25, 363 (1975).
- 102 K.N. Tu, "Interdiffusion in Thin Films: *Annual Review of Materials Science*, ed. by R.A. Huggins, 15, 147-176 (1985).
- 103 J.R. Abelson, K.B. Kim, D.E. Mercer, C.R. Helms, R. Sinclair, and T.W. Sigmon: Disordered intermixing at the platinum:silicon interface demonstrated by highresolution cross-sectional transmission electron microscopy, Auger electron spectroscopy, and MeV ion channeling. J. Appl. Phys. 63, 689 (1988).
- 104 Lin Zhang and Douglas G. Ivey: Prediction of Silicide Formation Sequence from the Principle of the Largest Free Energy Degradation Rate, in *Phase transformations in thin films: thermodynamics and kinetics.* Symposium held April 13-15, 1993, San Francisco, California, U.S.A. / editors M. Atzmon, (Pittsburgh, PA.: Materials Research Society, c1993), 299.
- 105 K.N. Tu and J.W. Mayer, Chap.10 in Thin Film-Interdiffusion and Reactions, ed. J.M. Poate, K.N. Tu, and J.W. Mayer, Wiley, New York, p359 (1978).
- 106 M-A Nicolet and S.S. Lau, Chap.6 in VLSI Electronics Microstructure Science, V6, ed. Norman G. Einsprunch and G. B. Larrabee, Academic Press, New York, p.329 (1983).
- 107 F.M. d'Heurle and P. Gas: Kinetics of formation of silicides: A review. J. Mater. Res. 1, 205 (1986).
- 108 G. Ottaviani: Metallurgical aspects of the formation of silicides. *Thin Solid Films* 140, 3 (1986).
- 109 F.M. d'Heurle, C.S. Petersson, J.E.E. Baglin, S.J. La Placa, and C.Y. Wong: Formation of thin films of NiSi: Metastable structure, diffusion mechanisms in intermetallic compounds. J. Appl. Phys. 55, 4208 (1984).
- 110 M. Diale, C. Challens and E.C. Zingu: Cobalt self-diffusion during cobalt silicide growth. *Appl. Phys. Lett.* 62, 943 (1992).

- 111 R. Pretorius, W. Strydom, and J.W. Mayer: Si tracer studies of the oxidation of Si, CoSi₂, and PtSi . *Phys. Rev.* B22, 1885 (1980).
- 112 A.P. Botha, and R. Pretorius: Co₂Si, CrSi₂, ZrSi₂ and TiSi₂ formation studied by a radioactive ³¹Si marker technique. *Thin Solid Films* 93, 127 (1982).
- 113 W.K. Chu, S.S. Lau, J. W. Mayer, H. Muller, and K.N. Tu,: Implanted noble gas atoms as diffusion markers in silicide formation. *Thin Solid Films* 25, 393 (1975).
- 114 T.G. Finstad: A Xe marker study of the transformation of Ni2Si to NiSi in thin films. *Phys. Status. Solid.* A63, 223 (1981).
- 115 M. Bartur and M.-A. Nicolet: Work function of Mo(110) in mixed cesium and cesium monoxide vapors. J. Appl. Phys. 54, 5404 (1983).
- 116 V.G. Weizer and N.S. Fatemi: Metal-silicon reaction rates-the effects of capping. *J. Elec. Mater.* 18, 7 (1989).
- 117 Lin Zhang and Douglas G. Ivey: A Novel Model For Solid State Reactions In Metal-Silicon Diffusion Couples, in Advanced metallization and processing for semiconductor devices and circuits--II : symposium held April 27-May 1, 1992, San Francisco, California, U.S.A. editors, Avishay Katz et al. (Pittsburgh, PA: Materials Research Society, 257 (1992.).
- 118 J.-K. Ahn, S.-G. Yoon, Characteristics of perovskite (Li_{0.5}La_{0.5})TiO₃ solid electrolyte thin films grown by pulsed laser deposition for rechargeable lithium microbattery *Electrochim. Acta* 50, 371 (2004).
- 119 J.-K. Ahn, S.-G. Yoon, Characteristics of Amorphous Lithium Lanthanum Titanate Electrolyte Thin Films Grown by PLD for Use in Rechargeable Lithium Microbatteries. *Electrochem. Solid State Lett.* 8, A75 (2005).
- 120 K. Kitaoka, H. Kozuka, T. Hashimoto, T. Yoko, Preparation of La_{0.5}Li_{0.5}TiO₃ perovskite thin films by the sol-gel method. J. Mater. Sci. 32, 2063 (1997).
- 121 J.-K. Ahn, S.-G. Yoon, C.S. Kim, Effect of $Li_{0.5}La_{0.5}TiO_3$ solid electrolyte films on electrochemical properties of $LiCoO_2$ thin film cathodes with different rapidthermal annealing conditions. *J. Vac. Sci. Technol.* B 23, 2089 (2005).
- 122 S.-I. Furusawa, H. Tabuchi, T. Sugiyama, S. Tao, J.T.S. Irvine, Ionic conductivity of amorphous lithium lanthanum titanate thin film. *Solid State Ionics*, 176, 553 (2005).
- 123 Cheng-Lung Liao Chung-Han Wen and Kuan-Zong Fung, The stabilit between perovskite $La_{2/3-x}Li_{3x}\Box_{1/3-2x}TiO_3$ (3x = 0.3) electrolyte and LiM_mO_n (M = Mn, Ni and Co) cathodes *Journal of Alloys and Compounds*, Vol. 432, 225, L22 (2007).

- 124 Shuhui Yu, Kui Yao, and Francis Eng Hock Tay, Observations and Analyses on the Thermal Stability of (1-x)Pb(Zn_{1/3}Nb_{2/3})O₃-xPbTiO₃ Thin Films. *Chem. Mater.* 19, 4373 (2007).
- 125 Y. Inaguma, L. Chen, M. Itoh, T. Nakamura, T. Uchida, M. Ikuta, M.Wakihara, High ionic conductivity in lithium lanthanum titanate. *Solid State Commun.* 86, 689 (1993).
- 126 A.G. Belous, G.N. Novitskaya, S.V. Polyanetskaya, Yu.I. Gornikov, Investigating complex oxides of the lanthanum lithium titanate (La_{2/3-x}Li_{3x}TiO₃) composition. *Inorg. Mater.* 23, 412 (1987).
- 127 Ryoichi Ohara, Tatsuo Schimizu, Kenya Sano, Masahiko Yoshiki and Takashi Kawakubo. Electrical Properties and Thermodynamic Stability of Sr(Ti_{1-x}, Ru_x)O₃ Thin films Deposited by Inductive-Coupling-Plasma-Induced RF Magnetron Sputtering. Jpn. J. Appl. Phys. Vol. 40, Part 1, No. 3A, 15 (2001).
- 128 S. D. Bu, M. K. Lee, C. B. Eom, W. Tian, X. Q. Pan, S. K. Streiffer, J. J. Krajewski. Perovskite phase stabilization in epitaxial Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ films by deposition onto vicinal (001) SrTiO₃ substrates. *Applied Physics Letter* Vol. 79, 3482 (2001).
- 129 C. B. Eom, R. B. Van Dover, Julia M. Phillips, D. J. Werder, J. H. Marshall, C.H. Chen, R. J. Cava, R. M. Fleming, and D. K. Fork, Fabrication and properties of epitaxial ferroelectric heterostructures with (SrRuO₃) isotropic metallic oxide electrodes. *Applied Physics Letters* Vol 63, 2570 (1993).
- 130 M.D. Rossell, O.I. Lebedev, G. Van Tendeloo, N. Hayashi, T. Terashima and M. Takano. Structure of epitaxial Ca₂Fe₂O₅ films deposited on different perovskite-type Substrates. J. Appl. Phys. Vol 95, 5145 (2004).
- 131 S. Ueno, J. Meng, N. Kamegashira, H. Saito-Nakano and K. Enami:Crystal structure of a layered perovskite, barium europium manganese oxide BaEu₂Mn₂O₇. *Materials Research Bulletin*. Vol, 31, No5, pp 497-502 (1996).
- 132 J.L. Fourquet, H. Duroy, and M.P. Crosnier-Lopez: Structural and Microstructural Studies of the Series La2/3-xLi3x□1/3-2xTiO3. J. Solid State Chem. 127, 283-294 (1996).
- 133 N. Nakayama and M. Takano, S. Inamura, N. Nakamishi and K. Kosuge:Electron microscopy study of the "cubic" perovskite phase $SrFe_{1-x}V_xO_{2.5+x}$ (0.05 $\leq x \leq 0.1$) *J. Solid State Chem.* 71, 403-417(1987).
- 134 J.C.H. Spence and J.M. Zuo: Bravais Lattice Determination, in *Electron Microdiffraction*, (Plenum Press. New York and London, 1992), p158.

- 135 B.F. Buxton and P.T. Tremewan: The atomic-string approximation in crossgrating high-energy electron diffraction. I. Dispersion surface and Bloch waves. *Acta Cryatallogr.* A36, 304 (1980).
- 136 J.A. Eades, Glide Planes and Screw Axes in CBED: The Standard Procedure, in Microbeam Analysis 1988, ed. D. Newbury, Sna Francisco Press, San Francisco, p.75 (1988).
- 137 R.C. Ecob, M.P. Shaw, A.J. Porter, and B.Ralph: The application of convergentbeam electron diffraction to the detection of small symmetry changes accompanying phase transformations II. Recrystallization of superalloys . *Philos. Mag.* A44, 1135 (1981).
- 138 P. Goodman: A Practical Method of three-dimensional space-Group analysis Using Convergent-Beam Electron Diffraction. *Acta Crystallogr.* A31, 793 (1975).
- 139 J.W Steeds, and R. Vincent: Use of High-Symmetry Sone Axes in Electron Diffraction in Determining crystal Point and Space Groups. J. Appl. Cryst. 16, 317 (1983)..
- 140 M. Tanaka, R. Saito and H. Sekii: Point-Group Determination by Convergent-Beam Electron Diffraction. *Acta Cryst.* A39. 357 (1983).
- 141 J.C.H. Spence and J.M. Suo: Symmetry Determination, in *Electron Microdiffraction*. (Plenum Press, New York and London 1992) p145.
- 142 A. R. West: Crystallography and Diffraction Techniques in *Basic Solid State Chemistry*. Chichester: John Wiley & Sons, c1999 Chapter 3, p125.
- 143 D. Williams and J. Goldstein: Principles of X-ray Energy-dispersive Spectrometry in the Analytical Electron Microscope in *Principles of Analytical Electron Microscopy* 1986, D.C. Joy, A.D. Romig Jr. and J.I. Goldstein ed. Plenum press. New York and London P123.
- 144 J.E. Wood, D.B. Williams, and J.I. Goldstein (1981), in "Quantitative Microanalysis with High Spatial Resolution", The Metal Soc., London, Book 277, p24-J. Microsc.133, 255(1984).
- R. Gauvin and G. L'Espérance : A Monte Carlo code to simulate the effect of fast secondary electrons on k_{AB} factors and spatial resolution in the TEM. J. Microsc. 168, Pt. 2, 153 (1992).
- 146 R. Gauvin : A parameterization of the Effects of Fast Secondary Electrons on Cliff-Lorimer k_{AB} factors. *Microbeam Analysis*, 1, 97 (1992).

- 147 E. Lifshin and R.Gauvin: Minimizing Errors in Electron Microprobe Analysis. *Microsc. Microanal.* 7, 168 (2001).
- 148 J.R. Michael, D.B. Williams, C.F. Klein and R. Ayer: The measurement and calculation of the X-ray spatial resolution obtained in the analytical electron microscope. J. Microsc. 160, 41 (1990).
- P.W. Hawkes: The Relation between the spherical aberration and distortion coefficients of electron probe-forming and project lenses. J. Phys. D: Appl. Phys. 1 No11, 1549 (1968).
- 150 P. Buseck, J. Cowley, L. Eyring, ed: *High-Resolution Transmission Electron Microscopy and Associated Techniques*, New York Oxford Oxford university Press 1988.
- 151 D. B. Williams and C. B Carter, in *Transmission Electron Microscopy a Textbook for Materials Science*, Plenum Press. New York and London, PP 463, 464, 465.
- 152 D. B. Chrisey and G. K. Hubler, ed: *Pulsed Laser Deposition of Thin Films*, John Wiley & Sons, 1994
- 153. P.J. Goodhew: Specimen Preparation for Transmission Electron Microscopy of Materials (Oxford ; New York: Oxford University Press ; Oxford : Royal Microscopical Society, 1984).
- 154. D.G. Ivey and G.R. Piercy: Cross-sectional TEM specimens of metal contacts to semiconductors. J. Elect. Microsc. Tech. 8, 233 (1988).
- 155 M.L. Post J.J. Tunney, and J. Yao, in *Chemical and Biological Sensors and analytical electrochemical Methods*, A.J. ricco, M.A.Butler, P. Wanysek, G.Horvai, and A.F.Silva, Editors, PV 97-19, p. 889, the Electrochemical Society Proceedings Series, Pennington, NJ (1977).
- 156 M.L. Post, J.J. Tunney, D. Yang, X. Du, and D.L. Singleton: Material Chemistry of Perovskite Compounds as Chemical Sensors. *Sensors and Actuators* B 59, 190 (1999).
- 157. K. Ichimura, Y. Inoue, I. Yasumori: Hydrogenation and Hydrogenalysis of Hydrocarbons on Perovskite Oxides; in *Properties and Applications of Perovskite-Type Oxides*, edited by L.G. Tejuca and J.L.G. Fierro (Marcel Dekker, New York, 1993), p.235.
- 158 B. Viswanathan: Co Oxidation and NO Reduction on Perovskite Oxides; in *Properties and Applications of Perovskite-Type Oxides*, edited by L.G. Tejuca and J.L.G. Fierro (Marcel Dekker, New York, 1993), p. 271.

- 159 D.E. Williams: Conduction and Gas Response of Semiconductor Gas Sensors, in *Solid State Gas Sensors*, edited by P.T. Moseley and B.C. Tofield (The Adam Hilger Series on Sensors, Bristol and Philadelphia, 1987), p.71.
- 160 K. Sahner, R. Moos, M. Matam, J.J. Tunney, and M.L. Post: Hydrocarbon Sensing with Thick and Thin Film p-type Conducting Perovskite Materials. Sensors and Actuators B 108, 102 (2005).
- 161 N. Barsan and U. Weimar: Conduction Model of Metal Oxide Gas Sensors. J. of *Electroceramics* 7, 143 (2001).
- 162 C. Xu, J. Tamaki, N. Miura, and N. Yamazoe: Grain Size Effects on Gas Sensitivity of Porous SnO₂-Based Elements. Sensors and Actuators B 3, 147 (1991).
- 163 D.E. Williams and K.F.E. Pratt: Microstructure Effects on the Response of Gas-Sensitive Resistors Based on Semiconducting Oxides. *Sensors and Actuators* B70, 214 (2000).
- 164 Z. Wang, T. Sasaki, N. Koshizaki, J.J. Tunney, and M.L. Post: Crystallized SeFeO_{3-x} Films Deposited by Pulsed Laser Deposition without in-situ Substrate Heating. *Thin Solid Films* 437, 95 (2003).
- 165 B.R. Sanders, J. Yao, and M.L. Post: Thin Films of SrFeO_{2.5+x} Effect of Preferred Orientation on Oxygen Uptake, in *Polycrystalline Thin Films*: *Structure, Texture, Properties and Applications*, edited by, K. Barmak, M.A. Parker, J.A. Floro, R. Sinclair, and D.A. Smith (Materials Research Society Symposium Proceedings 343, San Francisco, U.S.A 1994), p.463.
- 166 O. Grudin, R. Minescu, L.M. Landsberger, M. Kahrizi, G. Frolov, J.D.N. Cheeke, S. Chehab, M. Post, J. Tunney, X. Du, D. Yang, and D. Segall: High-Temperature Gas Sensor Using Perovskite Thin Films on a Suspended Microheater. J. Vac. Sci. Tecnol. A 20(3), 1100 (2002).
- 167 M. Ohring, in *Material Science of Thin Films*, 2nd ed. (Academic Press, San Diego, 2002), p. 682.
- 168 D.K. Fork: Epitaxial Oxides on Semiconductors, in *Pulsed Laser Deposition of Thin Films*, edited by D.B. Chrisey and G.K. Hubler (John Wiley and Sons, Inc., New York, 1994), Chapter 16.
- 169 P.J. Goodhew: Specimen Preparation for Transmission Electron Microscopy of Materials (Oxford; New York: Oxford University Press; Oxford: Royal Microscopical Society, 1984).

170 D.G. Ivey and G.R. Piercy: Cross-sectional TEM specimens of metal

contacts to semiconductors. J. Elect. Microsc. Tech. 8, 233 (1988).

- 171 C.N.R. Rao, J. Gopalakrishnan, and K. Vidyasagar: Superstructures, ordered defects, and nonstoichiometry in metal oxides of perovskite and related structures. *Indian Journal of Chemistry*, 23A, 265 (1984).
- 172 O.T. Sorensen: Thermodynamics and Defect structure of Nonstoichiometric Oxides, in *Nonstoichiometric Oxides*, edited by O.T. Sorensen (Academic Press, New York, 1981), Chpter 1, p. 1
- 173 LeRoy Eyring: Structure, Defects, and Nonstoichiometry in Oxides: An Electron Microscopic View, in *Nonstoichiometric Oxides*, edited by O.T. Sorensen (Academic Press, New York, 1981), p.338.
- 174 J.S. Anderson: The Real Structure of Defect Solids, in *Defects and Transport in Oxides*, edited by M.S. Seltzer and R.I. Jaffe (Plenum Press, New York, 1974), p. 25.
- 175 R.J.D. Tilley: Defect Crystal Chemistry and its Applications, in *Chemical Physics of Solids and Their Surfaces* Vol 8, edited by M.W. Roberts and J.M. Thomas (Royal Society of Chemistry, London, 1980), p. 121.
- 176 C.N.R. Rao and G.V. Subba Rao: Electrical conduction in metal oxides. *Physica Status Solid* A1, 597 (1970).
- 177 K. Sahner, R. Moos, M. Matam, J.J. Tunney, and M.L. Post: Hydrocarbon Sensing with Thick and Thin Film p-type Conducting Perovskite Materials. *Sensors and Actuators* B 108, 102 (2005).
- 178 N. Barsan and U. Weimar: Conduction Model of Metal Oxide Gas Sensors. J. of Electroceramics 7, 143 (2001).
- 179 C. Xu, J. Tamaki, N. Miura, and N. Yamazoe: Grain Size Effects on Gas Sensitivity of Porous SnO₂-Based Elements. *Sensors and Actuators* B 3, 147 (1991).
- 180 D.E. Williams and K.F.E. Pratt: Microstructure Effects on the Response of Gas-Sensitive Resistors Based on Semiconducting Oxides. *Sensors and Actuators* B 70, 214 (2000).
- 181 Z. Wang, T. Sasaki, N. Koshizaki, J.J. Tunney, and M.L. Post: Crystallized SeFeO_{3-x} Films Deposited by Pulsed Laser Deposition without in-situ Substrate Heating. *Thin Solid Films* 437, 95 (2003).
- 182 B.R. Sanders, J. Yao, and M.L. Post: Thin Films of SrFeO_{2.5+x} Effect of Preferred Orientation on Oxygen Uptake, in *Polycrystalline Thin Films: Structure, Texture, Properties and Applications*, edited by, K. Barmak, M.A. Parker, J.A. Floro, R. Sinclair, and D.A. Smith (Materials Research Society Symposium Proceedings 343, San Francisco, U.S.A 1994), p.463.
- 183 D. Wang, J.J. Tunney, X. Du, M.L. Post and Raynald Gauvin: Transmission electron microscopy investigation of interfacial reactions between SrFeO₃ thin films and silicon substrates. *J. Mater. Res.*, Vol.22, No1, 76(2007).
- 184 M.H. Loretto, *Electron Beam Analysis of Materials*, (Chapman and Hall, London 1984), p 88.
- 185 B.F. Buxton, J..A. Eades, J.W. Steeds, and G.M. Rackham: The Symmery of Electron Diffraction Zone Axis Patterns. *Philos. Trans. R.Soc. London, Ser. A.* 281,171 (1976).
- 186 Lange's Handbook of Chemistry (15th Edition) Edited by J.A. Dean, McGraw-Hill, 1999, p528.
- 187 P.T. Moseley and A.J. Crocker, *Sensor Materials* (Institute of Physics Publishing Bristol and Philadelphia. 1996). Chapter 4.
- 188 P.T. Moseley: Solid State Gas Sensors, *Measurement Science and Technology*.8. 223(1997).
- 189 J. Mizusaki, M. Okayasu, S.Yamauchi, and K. Fueki: Nonstoichiometry and phase relationship of the SrFeO_{2.5}. SrFeO₃ system at high temperature. *Journal of Solid State Chemistry*, 99, 166(1992).