# Investigation of InSb Thin Films Prepared by a Multilayer Vacuum Method

by

Wai-Wing Malcolm Lam

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Engineering

November, 1993

Department of Electrical Engineering McGill University Montreal, Canada Investigation of vacuum deposited InSb thin films

.

•

• .

# ABSTRACT

Thin films of InSb are important for modern electronic applications. When these films are prepared by vacuum evaporation, a precise control of the substrate and source temperatures is needed to obtain the required stoichiometry. It is therefore interesting to study a simplified vacuum evaporation method which does not need the precise control of substrate and source temperatures.

In the present work, a thermal evaporation technique has been adopted for the deposition of the Sb/In metallic sandwich layers. The composition of the films was controlled by regulating the amount of elemental material introduced to the boats. Using this method, multilayer films of Sb/In have been deposited sequentially on glass or (111) oriented single crystal silicon substrates with no intentional substrate heating. After the deposition, the films were treated either in an open tube environment, an ampoule or a vacuum system.

Effects of different heat treatment conditions on the physical and electrical properties of the films were studied. XRD results revealed that the films treated in vacuum had a polycrystalline structure. The films deposited on glass substrates and treated at temperatures between 490°C and 530°C had a highly oriented structure with a preferred (111) orientation. A room temperature Hall mobility of 18,000 cm<sup>2</sup>/V-sec was found for the films treated at 520°C. Study of magnetoresistance effect shows the close agreement

j

with theory by assuming that lattice scattering is the dominant scattering mechanism. Crystal grains with an average diameter of about 7  $\mu$ m were obtained on 11.5  $\mu$ m thick films.

)

# RÉSUMÉ

Des films minces de SbIn sont important pour les applications électroniques modernes. Quand les films sont préparés par méthode d'évaporation, un contrôle précis des températures de substrate et de source permet d'obtenir la stoechiométrie requise. Il est ainsi intéressant d'étudier une méthode d'évaporation simplifiée sans le besoin d'un contrôle précis des températures de substrate et de source.

Dans le travail, une technique d'évaporation thermique a été adoptée pour la déposition des couches Sb/In métalliques en sandwich. La somme des éléments de matière introduite pur bateaux permet de contrôle la composition des films. En utilisant cette méthode, des films à plusieurs couches de Sb/In ont été déposés alternativement sur des substrats en verre ou en monocrystal de Si sans chauffage de substrat. Après la déposition, les films sont traités thermiquement dans un tube ouvert, une ampoule ou un système à vide.

Les effets de recuit à des conditions différentes sur les propriétés physiques et électriques des films sont ensuite étudiés. Les résultats de XRD ont révélé que les films traités dans le vide avaient une structure polycrystalline. Les films déposés sur des substrats en verre et traités à des températures entre 490°C et 530°C ont des orientations préférentielles suivant la direction (111). Les résultats des effets Hall ont été mesurés pour obtenir la mobilité à 300°K. Les resultats obtenus pour la mobilité

iii

sont aussi élévés que 18000 cm<sup>2</sup>/V-sec dans les films traités à 520°C. Des données expérimentales ainsi suggèrent que l'eparpillement de réseau est dominant de l'étude d'effet de magnétoresistance. On obtient alors des grains de crystal avec un diamètre moyen d'environ 7  $\mu$ m sur les films d'épisseur de 11.5  $\mu$ m.

# ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to his supervisor, Dr. I. Shih, for his guidance throughout this study.

Thanks are also offered to Dr. C. X. Qiu for her help in solving practical problems and to Mr. L. S. Yip and Mr. S. N. Qiu for their helpful discussions.

Special thanks are given to Mr. Pham for translating the abstract into French.

The author is specially grateful to his family for their encouragement.

# TABLE OF CONTENTS

ABSTRACI			i
RÉSUMÉ			iii
ACKNOWLE	DGEMEN	ITS	v
Chapter	1	INTRODUCTION	1
Chapter	2	PROCEDURES OF THIN FILM DEPOSITION AND ANNEALING	5
	2.1. 2.2. 2.3. 2.4.	<pre>INTRODUCTION PRINCIPLE OF VACUUM EVAPORATION AND VACUUM EVAPORATION SYSTEM ANNEALING SYSTEM PREPARATION OF THIN FILMS 2.4.1. Etching of source materials 2.4.2. Preparation of Mo boats 2.4.3. Cleaning and preparation</pre>	5 8 10 10 10 11 11 11 13 14
Chapter	apter 3 CHARACTERIZATION TECHNIQUES OF THIN FILMS		23
	3.1. 3.2. 3.3. 3.4. 3.5. 3.6. 3.7. 3.8.	INTRODUCTION X-RAY DIFFRACTION CONDUCTION TYPE DETERMINATION CONDUCTIVITY MEASUREMENTS HALL EFFECT MEASUREMENTS STUDY OF MAGNETORESISTANCE EFFECT SCANNING ELECTRON MICROSCOPY ELECTRON MICROPROBE	23 24 25 26 27 31 32 34

Chapter	4	RESULTS AND DISCUSSION	48
	4.1. 4.2. 4.3. 4.4. 4.5.	INTRODUCTION RESULTS OF OPEN TUBE NITROGEN ANNEALING COMPOSITION ANALYSIS THICKNESS ESTIMATION THE GROUP D4 SAMPLES 4.5.1. X-ray diffraction results 4.5.2. Surface morphology 4.5.3. Conduction type 4.5.4. Room temperature conductivity 4.5.5. Hall effect measurements 4.5.6. Temperature dependence of conductivity	48 49 50 51 53 53 53 53 54 56
	4.6.	RESULTS OF X-RAY DIFFRACTION AND SURFACE	56
MORPHOLOGY FOR INSE THIN FILMS DE ON (111) ORIENTED SI WAFER 4.7. INSE THIN FILMS PREPARED BY THE T LAYER METHOD 4.8. MAGNETORESISTANCE EFFECT MEASUREM 4.9. STUDY OF THE INTERDIFFUSION BETWE		MORPHOLOGY FOR INSD THIN FILMS DEPOSITED ON (111) ORIENTED SI WAFER INSD THIN FILMS PREPARED BY THE THREE LAYER METHOD MAGNETORESISTANCE EFFECT MEASUREMENTS STUDY OF THE INTERDIFFUSION BETWEEN	57 58 60
<b>61</b>	_	In AND Sb	63
Chapter	5	CONCLUSIONS	91
Appendix	A	PHOTOLITHOGRAPHY PROCESS	95
KEFERENCE	5		96

# Chapter 1

# INTRODUCTION

Fabrication of electronic devices such as infrared devices, Hall effect devices and magnetoresistance devices often requires semiconductors with high carrier mobility, small band gap, and high magnetic sensitivity. Of the various potential candidates, the semiconductor indium antimonide (InSb) appears to be one of the most promising materials for these applications.

Single crystal InSb has energy gaps of 0.18, 0.23 and 0.235 eV at 300 K, 80 K and 4 K respectively. For InSb crystallized in a cubic structure, the lattice parameter  $(a_{0})$  is 6.47877 Å with a density of 5.7751  $g-cm^{-1}$ .<sup>1</sup> For the tetragonal structure, the corresponding lattice parameters are  $a_1 = 5.862$  Å and  $b_2 = 3.105$  Å with a density of 7.3 g-cm<sup>-3</sup>.<sup>1</sup> Estimates of effective mass for electrons at the conduction band minimum usually lie between  $0.013m_{\odot}$  and  $0.015m_{\odot}$  (m<sub>o</sub> being the free-electron mass).<sup>2</sup> The corresponding quantity for heavy holes is 0.18m. Evidence suggests that the light-hole effective mass is close to that of the electron effective mass.' The density of intrinsic carriers at 300°K is 2x10<sup>16</sup> cm<sup>-</sup>. The highest mobility reported for electrons in single crystal InSb is  $1.2 \times 10^{6}$  cm<sup>2</sup>/V-sec at  $80^{\circ}$ K and  $1 \times 10^{5}$  cm<sup>2</sup>/V-sec at  $300^{\circ}$ K,<sup>1</sup> whereas the highest mobility reported for holes in single crystal InSb is 7x10<sup>3</sup> cm<sup>2</sup>/V-sec at 77°K and 1.7x10<sup>3</sup> cm<sup>2</sup>/V-sec at 300°K.<sup>1</sup>

Single crystal InSb has been widely studied and reported in

the literature. However, for most applications, thin films of InSb are needed. Various methods have been used to prepare thin films of InSb, such as magnetron sputtering, ''' vapour phase transport reaction, ' vacuum evaporation (including co-evaporation and flash evaporation), ''' molecular beam epitaxy (MBE), '''' and metalorganic chemical vapour deposition (MOCVD).'' Thin films of InSb with a carrier mobility comparable to that of bulk single crystals are usually obtained by epitaxial growth using MBE method on single crystal substrates. The costs of single crystal substrates and the costs associated with the MBE method, however, are still high. For this reason, it would be profitable to study and develop low cost procedures (such as vacuum evaporation) for producing high quality InSb thin films. Recently, Okimura et al reported a room temperature electron mobility of 6x10<sup>4</sup> cm<sup>2</sup>/V-sec for InSb films prepared by vacuum evaporation on mica substrates.'<sup>4</sup>

Maintaining stoichiometry of the deposited compounds in thin films of InSb produced by conventional vacuum evaporation techniques with polycrystals and single crystals as sources is difficult. This is because of the large vapour pressure differences between In and Sb. A loss of volatile Sb was observed in most of the cases. In order to solve this problem, co-evaporation of elemental materials with separate source temperature control has been employed.<sup>18,20</sup> In addition, a precise control of substrate temperature was needed to obtain large crystal grains.

In 1954, Brentano et al reported the formation of InSb at room temperature by employing alternate evaporations of In and Sb thin

layers." However, no details of the crystallinity and electrical properties of InSb films has been reported by Brentano et al. Nadkarnı et al (1975) studied and reported some electrical properties for InSb thin film magnetoresistors fabricated on chromium-coated glass substrates.<sup>17</sup> By sequentially evaporating a single Sb layer followed by a single In layer, and heat treating the metallic films, polycrystalline InSb films were formed. Nevertheless, no details concerning the effects of the different heat treatment conditions on the crystallinity and electrical properties of the films deposited by sequential evaporation of Sb and In were reported. The above literature survey suggests that the sequential evaporation of Sb and In followed by proper heat treatment could be an efficient method of preparing InSb thin films. It might also be beneficial to evaporate several layers of Sb and In alternately to enhance the crystallization of InSb films during the annealing process.

In the present work, experiments have been carried out to produce and to study thin films of InSb on glass and (111) oriented single crystal Si substrates. A thermal evaporation technique has been employed for the deposition of the Sb/In metallic sandwich layers onto the substrates with no intentional substrate heating. It was thought that a simplified vacuum evaporation method, one that does not require precise control of source and substrate temperature would be most interesting to develop. The composition and thickness of the films was controlled by regulating the amount of elemental material introduced to the Mo boats. Following the

deposition, heat treatment was carried out either in an open tube environment, an ampoule or a vacuum system to crystallize the InSb thin films. The effects of different annealing conditions on the physical and electrical properties of the films were studied.

The arrangement of this thesis is as follows: In Chapter 2, the principles of vacuum evaporation are first introduced, the vacuum evaporation unit and annealing systems used in the present study are described and the procedure for film preparation is presented. The various characterization techniques used are described in Chapter 3. In Chapter 4, the results from various characterizations of the InSb thin films are discussed in detail. Finally, in Chapter 5, main conclusions are dispensed.

## Chapter 2

# PROCEDURES OF THIN FILM DEPOSITION AND ANNEALING

#### 2.1. INTRODUCTION

Vacuum evaporation is one of the most effective and least expensive methods utilized for the deposition of high quality thin films. In the present work, thin films of InSb were prepared on glass and (111) oriented single crystal p-S1 substrates.

By using a simple vacuum evaporation method, elemental metallic sandwich layers were deposited on the substrates. In order for the interdiffusion of In and Sb to occur, the samples were heat treated in a furnace. The heat treatment is either taken place in a nitrogen environment, evacuated ampoules, or vacuum system. In this study, most of the samples were treated in vacuum.

In this chapter, the principles of vacuum evaporation, structures of vacuum evaporation system, annealing system, and film preparation are described.

#### 2.2. PRINCIPLE OF VACUUM EVAPORATION AND VACUUM EVAPORATION SYSTEM

When the molecules are more densely packed, intermolecular collisions occur more frequently. The average distance travelled by a gas molecule between successive collisions is called the mean free path  $(\lambda)$ . There are standard derivations in Kinetic Theory for evaluating the mean free path. Here it is only necessary to quote

the result $^{35}$ 

$$\lambda = \frac{1}{\sqrt{2\pi\sigma^2 n}} \qquad \dots \qquad (2.1)$$

where  $\sigma$  is the molecular diameter, n is the number of molecules per unit volume, and  $\lambda$  is the mean free path. As  $\lambda$  is proportional to 1/n and pressure in a closed system is proportional to n, it Table 2.1. Kinetic Theory Data for Air at 20 c follows that the mean free path for Air Mean free path (torr) Mean free path (torr)

pressure. Thus, it is clear that the lower the pressure, the longer the mean free path.

In a vacuum evaporation system, with a sufficiently low

Pressure	Mean free path
(torr)	(cm)
760	6.5x10 <sup>-1</sup>
1	5 x10 <sup>-1</sup>
10 <sup>-3</sup>	5 x10 <sup>11</sup>
10 <sup>-3</sup>	5 x10 <sup>11</sup>
10 <sup>-3</sup>	5 x10 <sup>11</sup>
10 <sup>-12</sup>	5 x10 <sup>11</sup>

pressure, the mean free path of the atoms leaving the hot source is much greater than the distance between the source and substrate. Thus, the material evaporated from a hot source can travel to the substrate unimpeded by the residual gas molecules in the vacuum system. Table 2.1 gives the approximate values of mean free path for different pressures of air at 20°C." In the current study, a typical base pressure of  $10^{-5}$  torr was used. Since the mean free path is inversely proportional to the pressure, we can estimate that the corresponding mean free path is about 500 cm from Table 2.1.

In the ongoing investigation, the vacuum evaporation system used was an Edward Coating System (model E306A). A schematic

diagram of the vacuum system is shown in Figure 2.1. The vacuum unit consists of a 12-inch glass chamber, a 4-inch diffusion pump, and a high efficiency rotary pump.

The rotary pump can be used to pump the vacuum chamber from atmospheric pressure to a pressure of few tens of millitorrs. It can also be used to maintain the low pressure environment required for the diffusion pump. The diffusion pump is used to achieve the high vacuum condition required for a large mean free path.

Inside the vacuum chamber, there is a sample holder for the substrates, two Mo boats used to contain the source materials, and a shutter. Although the vacuum system is capable of handling two boats simultaneously, only one boat can be heated at a time. When there is a sufficiently good vacuum (e.g. 10<sup>-5</sup> torr or less), a current is allowed to flow through the boat, the boat becomes a resistive heater. Upon reaching a sufficiently high temperature, the source material contained in the boat will vaporize i.e. become free atoms. The free atoms will vaporize in every direction. Some of the free atoms will finally affix to the substrates.

The amount of materials needed for a certain film thickness can be estimated by a simple method. First of all, we assume that the free atoms leaving the hot source will vaporize in every direction within a semi-hemisphere. The volume of a semi-hemisphere can be obtained by equation (2.2), where r is the radius of the

$$V = \frac{2}{3}\pi r^3$$
 .....(2.2)

semi-hemisphere or more practically it is the distance between the source materials and the substrates, and V is the volume of the semi-hemisphere. If we express (2.2) in the differential form, the equation becomes

### $dV=2\pi r^2 dr \qquad \dots \dots (2.3)$

where dV and dr become the differential change in volume and radius respectively. Equation (2.3) is accurate if dr is small compared to r. We can interpret dr as the thickness of the film to be deposited. From (2.3), we can estimate the volume of the source material (dV) needed for a given film thickness (dr). Figure 2.2 shows a schematic diagram of the above described situation.

Once we obtained the volume of material needed (dV), we can calculate the mass of source material needed by the following simple relation,

#### $m=V\rho$ .....(2.4)

where V is equivalent to the value of dV,  $\rho$  is the density of the source material, and m is the mass of the source material required. We can therefore control the thickness of the deposited films by adjusting the mass of the source material introduced into the boat.

#### 2.3. ANNEALING SYSTEM

Several annealing schemes with different temperature cycles were employed in the current study. Three annealing schemes used are listed below. Temperature cycles will be described in Section 2.4.

- (1) Heat treat the samples in an open tube furnace with flowing  $N_2$  gas.
- (2) Seal the sample in an evacuated glass ampoule, heat treat in furnace.
- (3) Put the sample inside a glass tube (one end sealed), which is pumped by a vacuum unit, insert the glass tube into the furnace and carried out the heat treatment.

Figure 2.3 (a), (b) and (c) show the corresponding schematic diagrams of the above three schemes.

The setups involved the use of a three-zone furnace in our laboratory. The heat treatment procedures were focused on the center zone of the furnace. A home made vacuum unit similar to the vacuum evaporation unit previously described was utilized in both the formation of ampoules and the vacuum heat treatment with a glass tube. The design of the pumping unit is almost the same. The only difference is the shape of the vacuum chamber. Instead of a bell jar, a long glass tube is utilized for annealing purposes and the formation of the ampoules.

In schemes (2) and (3), the glass tube with the sample inside was pumped to a pressure of about  $5\times10^{-4}$  torr. For scheme (2), once the desired pressure was reached, a hand held torch was used to melt the glass tube until the ampoule was sealed and detached from the rest of the tube. For scheme (3), the vacuum pumped glass tube with the sample in the tip was pushed to the center of the furnace to carry out the heat treatment process. The pumping was continued until the heat treatment process was completed.

#### 2.4. PREPARATION OF InSb THIN FILMS

The preparation of InSb thin films includes surface etching of the source materials, preparation of Mo boats, cleaning of substrates, vacuum evaporation of Sb/In metallic sandwich layers, annealing, and patterning of the films by a photolithography technique.

## 2.4.1. Etching of source materials

High purity (99.999%) Indium and Antimony shots were used as the starting materials. However, since the materials have been exposed to the atmosphere for a long time, thin layers of oxides are likely to have formed on the surface of the metal shots. In order to improve the quality of the evaporated metal films, etching of the surface oxides is necessary. This etching was done by immersing the metal shots into an etchant which consisted of 1 part  $HNO_3$ , 1 part HCl, and 8 parts  $H_2O$ . The metal shots were allowed to etch for about 1 minute, until the surface of the metal shots became shiny.

### 2.4.2. Preparation of Mo boats

Mo boats were used as the heating sources. The boats were made from strips of 0.005" thick Mo sheets with an area of about  $1\times12$  cm<sup>2</sup>. The strips were shaped into rectangular boats. Figure 2.4 shows a photograph of a typical Mo boat used in our study. Before installing the Mo boats in the vacuum system, it is necessary to etch the boats. This procedure increases the electrical resistances

and at the same time cleans the surface of the boats. The etching was done by immersing the U-shape part of the boat into an etchant which consisted of 1 part  $HNO_3$ , 3 parts HCl, and 4 parts  $H_2O$ . Finally, the boats were rinsed with  $H_2O$  and wiped dry.

2.4.3. Cleaning and preparation of substrates

Two different kinds of substrates were used in this study. (1) Plain microscope glass slides with an area of 75x25 mm<sup>2</sup>.

The glass substrates were immersed in a hot solution of biodegradable soap for 10 minutes, then rinsed with  $H_2O$ , and wiped dry. Next, the glass substrates were immersed into the mixture of 1 part of HNO<sub>3</sub> and 3 parts of HCl for about 10 minutes. Finally, the substrates were rinsed with  $H_2O$  and wiped dry.

(2) (111) oriented p-Si wafers with a diameter of 1.5".

The wafers were immersed into a beaker of TCE. The beaker was put into a ultrasonic bath for 10 minutes. After this step, the wafer was transferred to a beaker of ACE and the above process was repeated. Finally, the wafers were rinsed with  $H_2O$  and spun dry.

2.4.4. Vacuum evaporation of Sb/In metallic sandwich layers

Multilayer films of Sb/In were deposited by using a thermal evaporation method in a vacuum system with a base pressure of about  $10^{-5}$  torr. The distance between the source materials and the substrates was about 10 cm. Weighted amount of Sb and In were

11

 $\mathcal{T}$ 

introduced into the two Mo boats and evaporated in one of the two sequences described below.

(1) The eight layer deposition method.

The materials were evaporated in the sequence of Sb, and then In. After the evaporation of In, the chamber was opened and some new materials were added to the two boats. This evaporation process was repeated three more times. Thus, metallic sandwich thin films consisting of eight metallic layers in alternating sequence of Sb and In were formed. The first layer from the substrate was Sb and the outermost layer was In. The order of depositing the films is important, because indium prevents the evaporation of the antimony during the annealing process.<sup>17</sup> Figure 2.5 (a) shows a cross sectional view of the as-deposited metallic films employing this eight layer deposition method.

It is important to mention that during the evaporation processes, the pressure inside the chamber was increased to approximately  $3\times10^{-5}$  torr. After the evaporation of Sb, before In could be evaporated, it was necessary to wait until the pressure inside the chamber decreased to the original base value.

There are some draw backs to the above mentioned deposition method. First of all, the first Sb layer deposited on the substrate tends to grow preferentially in a circular manner. This leads to an inhomogeneous deposited films. Figure 2.6 shows a photograph of a sample with preferential

growth of the Sb layer. Second, since the vacuum chamber has to be opened for three times before the deposition is complete, oxidation of the exposed indium layer is possible. To eliminate the above weaknesses, the three layer method was developed.

(2) The three layer deposition method.

This method involved the deposition of materials in the order of In, Sb, then finally In. The entire deposition process was completed without breaking the vacuum at any time. First, a thin layer of In was evaporated. The thickness of this thin layer was several hundreds of angstroms. The In layer can act as a nucleating agent for the Sb layer. Thus preferential growth of Sb can be eliminated. Following the deposition of this thin In layer, Sb and In were evaporated sequentially. Figure 2.5 (b) shows a schematic cross sectional view of a sample deposited by the three layer method.

#### 2.4.5. Annealing of Sb/In metallic sandwich thin films

The interdiffusion of In and Sb takes place when the samples have been heated to a substantially high temperature. During the annealing, In and Sb atoms will chemically combine and yield InSb compound.

Vacuum deposited samples were cut into appropriate sizes and heat treated using one of the annealing schemes described in Section 2.3. The heat treatments were subject to one of the two different temperature cycles defined below.

- (1) The center zone of the furnace was preheated to a desired temperature (e.g. 500°C). The temperature of the two side zones were kept at 250°C. Then, either a quartz boat containing sample, an ampoule, or a vacuum glass tube was pushed into the center zone in two steps. The time interval between steps was 1 minute. The sample was allowed to stay in the furnace for 15 minutes. Finally, the sample was pulled out by reversing the pushing procedure and was permitted to cool down to room temperature.
- (2) This heat treatment cycle was only applied in the ampoule and vacuum tube schemes. In this cycle, the sample was pushed to the center zone at room temperature before the furnace was turned on. The furnace was then allowed to heat up. Once the temperature reached 500°C, the temperature was maintained for 15 minutes. The furnace was turned off. The sample was pulled out when the temperature of the center zone decreased to about 150°C. As a result, a typical annealing cycle similar to the one shown in Figure 2.7 was complied.

After the annealing process, crystallized InSb thin films were obtained. Fig. 2.5 (c) shows the cross sectional view of the crystallized InSb thin film after the heat treatment.

2.4.6. Patterning of the films by a photolithography technique

The details of the photolithography step carried out in this study is outlined in Appendix A. However, it is important to mention the shape of the photomask and the etchant used here.

Since Hall effect measurements were to be carried out, a photomask with the bridge shape shown in Figure 3.4 was used. A positive photoresist was used with the photomask to create the desired pattern. A wet chemical etching process was employed. The etchant used to etch the treated samples consisted of 1 part of HNO<sub>3</sub>, 1 part of HCl, and 4 parts of H<sub>2</sub>O. The etching rate was about 4.5  $\mu$ m/minute. Therefore, the etching time was approximately 24 seconds for a film of about 1.8  $\mu$ m thick. Details of the Hall effect measurements will be described in Chapter 3.



Fig. 2.1. A schematic diagram of an Edward Coating System (model E306A).



Fig. 2.2. A diagram clarifying the relation between dr and r.



Fig. 2.3. Schematic diagrams of different annealing schemes. (a) Open tube method, (b) ampoule method, and (c) vacuum tube method.



Fig. 2.4. A photograph of a typical Mo boat used in the vacuum evaporaticn process.



(a)







(C)

Fig. 2.5. Schematic views of two as-deposited films and a film after heat treatment. (a) As-deposited film using the eight layer deposition method, (b) as-deposited film using three layer deposition method, and (c) InSb thin film after heat treatment.



ς.

Fig. 2.6. A photograph showing the preferential growth of a Sb thin film deposited on a glass substrate. The vertical bar represents 400 µm.



Fig. 2.7. Temperature as a function of time for the annealing cycle 2.

# CHARACTERIZATION TECHNIQUES OF THIN FILMS

Chapter 3

#### 3.1 INTRODUCTION

In this chapter, the characterization techniques employed in the study of InSb thin films are delineated. These include the extraction of common physical and electrical parameters, such as crystal structure, conduction type, electrical conductivity, carrier concentration, carrier mobility, and Hall coefficient. Crystalline quality of InSb thin films was examined by X-ray diffraction. Conduction type was determined by the hot probe method and confirmed by Hall effect measurements. Conductivities of the films was determined from the bridge pattern obtained in the chemical etching step. Carrier concentrations, carrier mobilities and Hall coefficients were determined by Hall effect measurements.

In addition, magnetoresistance effects were studied to better understand the film properties. Atomic composition of the films treated at different temperatures was studied by electron microprobe. Furthermore, scanning electron microscopy (SEM) was employed to measure the thicknesses of the films and observe the interdiffusion of metallic thin films.

#### 3.2 X-RAY DIFFRACTION

X-ray diffraction is an effective method for determining the

crystalline structure of thin films. It is a nondestructive and non-contact process which reveals information on the presence of phases, on film thickness and grain size.<sup>37,38</sup> The schematic diagram of an X-ray diffractometer is shown in Figure 3.1.

The X-ray diffractometer consists of a goniometer to rotate the sample, an X-ray tube to produce radiation, and a counter to detect the radiation spectrum emitted by the sample. The radiation spectrum is then transformed into a pulse spectrum. After amplification, the pulse spectrum can be converted into a graphical record of intensity versus diffraction angle.

The fundamental equation for the maximum diffraction is the Bragg's law

$$2d_{hkl}\sin\theta = n\lambda \qquad \dots \qquad (3.1)$$

where n is an integer,  $\lambda$  is the wavelength of the incident X-ray,  $d_{nkl}$  is the spacing between the crystal planes, and  $\theta$  is the incident angle. The scattered waves interfere with each other and the maximum intensity is reached when the Bragg condition is satisfied. From the diffraction pattern, the incident angles  $\theta$  at which there is a maximum diffraction can be obtained. The corresponding d values can be calculated from the equation. The crystal structure of the film can then be determined from the ASTM data.

A Siemens X-ray diffractometer was used in the present work. The sample to be examined was mounted on a glass sample holder with double-sided scotch tape. The sample holder was then put into the goniometer and the measurements were carried out. The diffraction

data was collected in a  $2\theta$  range between  $15^{\circ}$  and  $80^{\circ}$ .

#### **3.3 CONDUCTION TYPE DETERMINATION**

The hot-probe method is a common technique for rapidly determining whether a semiconductor is n- or p-type. The only equipment required for performing the hot-probe measurement is a hot probe, a cold probe, and a sensitive voltmeter. In our case, the hot probe is simply a low temperature soldering iron; the cold probe is a typical metal probe. A schematic diagram of the hotprobe setup is shown in Figure 3.2. The measurement procedure is extremely simple. After allowing the hot probe to heat up to between 40°C and 50°C, the two probes are brought into contact with the semiconductor sample The voltmeter can detect the potential drop across the two probes, the sign of the potential drop indicating the semiconductor type. The spacing between the probes is set arbitrarily and can be reduced to enhance the voltmeter reading.

A simplified explanation of how the hot probe method works is presented in Figure 3.3. In the vicinity of the probe contact, the hot probe creates an increased number of high-energy carriers. These energetic carriers are predominantly holes in the case of a p-type material and electrons in an n-type material. With more energetic carriers near the hot probe than elsewhere, diffusion acts so as to spread the higher energy carriers throughout the sample. The net effect is a deficit of holes or a net negative charge in the vicinity of the hot probe for a p-type material, and

a positive charge buildup near the hot probe within an n-type material. Accordingly, a negative voltage will be observed on the hot probe end if the material is p-type, and a positive voltage will indicate an n-type material.

#### **3.4 CONDUCTIVITY MEASUREMENTS**

In this section, a conductivity measurement method which can be used in both room temperature and low temperature ranges is described. The measurements were made after the patterning of the films. Figure 3.4 shows the photomask used in the patterning procedure. There are six electrodes, the two largest electrodes (e and f) were used to supply a small dc current (I), either electrode pair (a and c) or (b and d) can be used to measure the voltage drop (V) across the thin film. With this configuration, the film becomes a resistor with length l, width w, and thickness t. The conductivity ( $\sigma$ ) of the film can be obtained from

where l is the separation between electrodes (a and c), w is the width of the etched film, and t is the thickness of the treated film. The photomask was designed such that l is 5 mm and w is 1 mm. The corresponding l/w ratio is 5.

Silver paste was used as the ohmic contacts to the electrodes. Thin copper wires were attached to the silver paste contacts before contacts dried. The voltage and current were measured by two HP model 3478A multimeters. A liquid nitrogen cryostat was utilized

to measure temperature dependent conductivity.

#### 3.5 HALL EFFECT MEASUREMENTS

Hall effect measurements can provide information on carrier concentration and mobility which are important parameters of a semiconductor.<sup>49,40</sup> When a sample with an electric current flowing in the z direction (with current density j) is placed in a magnetic field (with magnetic inductance  $B_{z}$ ), which is perpendicular to the direction of the current flow, a Lorentz force will be created in the direction normal to the current and magnetic field plane subject to the type of carriers. If we assume the semiconductor is n type, the electric field created by the Lorentz force is the Hall electric field ( $E_y$ ) which can be expressed as

$$E_{\mathbf{y}} = R_{\mathbf{H}} B_{\mathbf{z}} j_{\mathbf{x}} \qquad \dots \qquad (3.3)$$

where  $R_{H}$  is defined as the Hall coefficient. A schematic diagram is shown in Figure 3.5 illustrating the coordinate system and the Hall effect for an n-type semiconductor. In the figure, point P and Q are at opposite ends of an equipotential line in the absence of a magnitude field. When magnetic induction  $B_{z}$  is applied, P has a positive potential relative to Q for an n-type semiconductor.

The physical significance of the Hall effect becomes apparent when a current is considered as a stream of electrons moving through a solid. An electron travelling with a velocity  $\mathbf{v}$  will experience a Lorentz force ( $\mathbf{B} \times \mathbf{v}$ ) q, where q is the charge of carrier. In free space, the electron will be deflected in a direction perpendicular to the plane of  $\mathbf{B}$  and  $\mathbf{v}$ , but the current
inside the solid will be confined within the boundaries of the solid. Some electrons will be deflected by **B** at first, but these will create an electric field which will counterbalance the Lorentz force acting on the carriers. Thus, the current continues to flow as before. The equation for this effect is given by

$$(\mathbf{B} \times \mathbf{v}) q = q\mathbf{E} \qquad \dots \dots (3.4)$$

Hence if  $\mathbf{v} = (V_{\lambda}, 0, 0)$  and  $\mathbf{B} = (0, 0, B)$ , then  $\mathbf{E} = (0, -E_{\lambda}, 0)$ . The relation between current density j and the electrons' velocity v (assumed to be the same for all electrons) is

$$j = nqv \qquad \dots \dots (3.5)$$

where n is the concentration of electrons. Hence from (3.4) and (3.5), we obtain

$$E_{y} = -\frac{1}{nq} B_{z} j_{x} \qquad \dots \dots (3.6)$$

So that the Hall coefficient defined by equation (3.4) is inversely proportional to the concentration of conduction electrons:

$$R_{H} = -\frac{1}{nq} \qquad \dots \qquad (3.7)$$

In these equations q denotes the magnitude of the electronic charge. The direction of  $E_y$  depends upon the sign of q. The convention is adopted that when q is negative  $R_{ll}$  is taken as negative, as in equation (3.7). Thus, it is clear that for an n-type semiconductor where electrons carrying negative charges are the predominant carriers,  $R_{ll}$  is negative. On the other hand,  $R_{ll}$  will be positive for a p-type semiconductor. Equation (3.7) gives us a simple relation between carrier concentration and Hall coefficient. However, more detailed studies showed that the R.H.S. of equation (3.7) should be multiplied by a numerical factor ( $\alpha$ ), but this value never departs very far from unity.<sup>49</sup> This deviation is due to the different scattering mechanisms presented in different materials. Thus equation (3.7) becomes

$$R_{H} = -\alpha \frac{1}{nq} \qquad \dots \qquad (3.8)$$

For InSb,  $\alpha$  lies between 1 and  $3\pi/8$  for temperatures between 200°K and 700°K.<sup>49</sup> For ease of calculation,  $\alpha$  is taken as 1 for all the calculations and data presented hereafter. This will result in an error of less than 20% which is not significant in most cases.

By knowing the Hall electric field, both Hall coefficient and hence electron concentration can be obtained. Moreover, if Ohm's law is obeyed, the current can be defined by writing

$$j_x = \sigma E_x \qquad \dots \dots (3,9)$$

where  $\sigma$  is the conductivity of the material. Thus, dividing equation (3.5) by equation (3.9), we get

where  $\mathbf{\mu}$  is defined as the carrier drift velocity per unit electric field, or mobility. The combination of equations (3.8) and (3.10) yields that very informative quantity, the mobility. It is a convention to regard  $\mu$  as a positive quantity regardless

.....(3.11)

.....().

the sign of  $R_{\rm H}$ . The carrier mobility defined by the above equation is called Hall mobility. In our case, the Hall mobility is assumed to be equal to the so-called conductivity mobility defined in equation (3.10).

 $\mu = |R_{\mu}| \sigma$ 

The measurement of Hall effect was relatively simple. Similar to the conductivity measurements, the two large electrodes (e, f) were used to supply a small dc current. Either electrode pair (a, b) or (c, d) was used to measure the Hall voltage. Practically, the Hall coefficient ( $R_{H}$ ) can be obtained by the following relation,

$$R_{H} = \frac{V_{H} t}{I B} \qquad \dots \qquad (3.12)$$

where  $V_H$  is the Hall voltage (the potential difference across the Hall electrodes), *B* is the magnetic induction, *I* is the current passing through the sample, and *t* is the thickness of the film. Figure 3.6 shows a schematic diagram of the measurement setup.

Theoretically, the Hall voltage should be zero in the absence of a magnetic field. In practice, however, it is possible to observe a voltage between the Hall electrodes even in the absence of a magnetic field. This is due to the misalignment of the Hall electrodes. Offsets have to be made when interpreting the results. For a more reliable result, the Hall voltage was measured and plotted as a function of applied current; the typical range of current used was between 0.1 mA and 10 mA. The data points were then fitted by a straight line passing through origin. The slope of the straight line  $\Delta V_{II}/\Delta I$  was used to replace the  $V_{II}/I$  term in

equation (3.12). As an example, figure 3.7 shows a typical plot made after measurement. Since there were two pairs of Hall electrodes, the average value of the two  $\Delta V_H/\Delta I$  values obtained using the two pairs of Hall electrodes was used in determining  $R_H$ . Taking the average reduces the error due to the inhomogeneity of the sample. Once we determined the value of Hall coefficient, the carrier concentration and mobility were obtained by (3.8) and (3.12) respectively.

For the liquid nitrogen temperature measurement, a specially designed plastic container was used. The sample was attached to the bottom of the container by means of silicone gel. Liquid nitrogen was poured into the container slowly to cool the sample. The container was then inserted into a space between the permanent magnets and measurements were carried out. Figure 3.8 shows the corresponding schematic diagram.

In our laboratory, a permanent magnet with a magnetic inductance of 1700 Gauss was used. The sample current and Hall voltage were measured by using two HP multimeters. Silver paste was used as the ohmic contact materials as in the conductivity measurement.

## 3.6 STUDY OF MAGNETORESISTANCE EFFECT

In the last section, the Hall effect phenomenon was described. The charge carriers experience a Lorentz force which modifies the travelling paths of the carriers. The result of this path deflection also leads to another phenomenon called the

magnetoresistance effect. Figure 3.9 is a schematic diagram demonstrating the effect of different carrier paths. In the diagram, the electrons are injected into the semiconductor on the left side. Upon applying a magnetic field  $B_{\rm e}$ , some of the charge carriers will be deflected. As a result, these electrons will experience scatterring and will have a longer, slower path. Thus, fast and slow paths co-exist in the semiconductor, leading to a reduction in conductivity.

In this project, work was concentrated on the transverse magnetoresistance effect (the direction of magnetic field is perpendicular to the current flow). The change in magnetoresistance  $(\Delta R/R_o)$  was studied as a function of (a) current, and (b) incident angle of the magnetic field ( $\beta$ ). (R<sub>o</sub> is the resistance in the absence of a magnetic field,  $\Delta R$  is the change of resistance upon applying a magnetic field.) A similar setup to the one used in the Hall effect measurements was employed. Figure 3.10 shows the arrangement of the measuring setup to measure angle dependent transverse magnetoresistance.

## 3.7 SCANNING ELECTRON MICROSCOPY

Scanning Electron Microscopy (SEM) has been used intensively for the analyzing of surfaces. SEM micrographs contain the threedimensional appearance of textured surfaces. When combined with the high resolution, an extensive magnification range, SEM is uniquely suited for the study of surfaces. In this section, the basic principle of SEM will be discussed.

The SEM consists of two major parts. An electronic console provides the switches and controlling knobs for adjusting the intensity of the image on the viewing screen, focusing, and photography. The electron column is where the electron beam is created, focused to a small spot, and scanned across the specimen to generate the signals that control the local intensity of the image on the viewing screen. To understand how this works, the parts of the electron column should be considered in more detail (see Figure 3.11).

- (1) Electron Gun. The electron gun, at top of the column, provides a source of electrons. Electrons are usually emitted from a hot tungsten filament and accelerated down the evacuated vacuum chamber. A vacuum is necessary because electrons can travel only very short distances in air.
- (2) Electron Lenses. Two or three electron lenses are used to focus the electron beam to a small spot about 5 nm - 50 nm ir diameter. Then the beam will finally pass through an objective lens before reaching the specimen. The function of the objective lens is to move the smallest cross-section of the beam up and down until it meets the specimen surface. This corresponds to a focused image.
- (3) Objective Aperture. This is a platinum disk with a small hole (about 100 µm diameter) in it and is often located inside the objective lens. Its function is to limit the angular width of the electron beam in order to reduce lens aberration effects and to improve depth-of-field in the image.

- (4) Specimen Chamber. This large evacuated space below the objective lens contains the specimen stage with all its motions, the electron signal detectors, the X-ray detector, and a pumping line connected to the main vacuum pump.
- Everhart-Thornley (E-T) Electron Detector. The E-T detector is (5) the most common type of detector for electron signals. The E-T detector is sensitive to both types of emitted signal-carrying electrons: backscattered electrons and secondary electrons. Low-energy secondary electrons are drawn toward the detector by а high voltage. The signal is amplified by а photomultiplier tube (PMT) to produce electrical signal that eventually modulates the intensity of the viewing CRT.
- (6) Vacuum System. For most SEMs, the vacuum is produced by a diffusion pump backed by a rotary mechanical pump. This pumping scheme provides a suitable environment for electron beams and signals.

A JOEL JSM 6100 scanning microscope was used in the current study.

## 3.8 ELECTRON MICROPROBE

The electron microprobe has been developed as an extremely powerful tool in spectrochemical analysis for a wide range of applications, ranging from qualitative elementary distribution studies, to highly localised quantitative analysis on a one micron scale.

The principle of the electron microprobe method is rather

simple. When an electron beam is accelerated to the surface of a metallic surface, a complex X-ray spectrum will be emitted. The spectrum is selectively analyzed by one or several spectrometers. Comparison between the intensities of the characteristic X-rays, emitted under identical experimental conditions by the sample and by a calibration standard (pure element), permits the determination of respective elementary mass concentrations. Thus, the atomic concentration can then be tabulated. The important elements of an electron microprobe are shown in Figure 3.12. The structure is very similar to that of a SEM.



Fig. 3.1. A schematic diagram of an X-ray diffractometer.







Fig. 3.3. A simplified explanation of how the hot-probe method works. (After Ref. 41)









Fig. 3.5. The Hall effect. (a) The relative direction of the current, magnetic induction and Hall field for negative electrons. (b) A strip of conducting material, edges parallel to the x and y directions. Points P and Q are at opposite ends of the equipotential in the absence of a magnetic field. When induction  $B_z$  is applied, P has a positive potential relative to Q (for negative electrons). (After Ref. 39)



Fig. 3.6. Setup for the room temperature Hall effect measurements.



Fig. 3.7. A plot of  $V_{\scriptscriptstyle H}$  versus I for sample D4-1.



Fig. 3.8. Setup for liquid nitrogen temperature Hall effect measurements.



Fig. 3.9. The magnetoresistance effect. Slow electrons tend to suffer a greater deflection than fast electrons. (After Ref. 39)



Current Flowing Direction: into the paper.





Fig. 3.11. Schematic diagram of the main working parts of a SEM. (After Ref. 42)



Fig. 3.12. Schematic diagram of the electron microprobe. (After Ref. 43)

# Chapter 4 RESULTS AND DISCUSSION

## 4.1 INTRODUCTION

The effects of different annealing conditions on the morphology and crystallinity of the InSb thin films deposited on different substrates will be described in this chapter. The actual measured thicknesses of the films deposited by the eight-layer and three-layer methods will be compared with the estimated values obtained from the mathematical model presented in Chapter 2. In addition, the atomic composition and electrical properties such as conduction type, conductivity, Hall mobility, Hall coefficient, carrier concentration and magnetoresistance effects for thin films deposited on glass substrates will be discussed. Finally, the SEM results concerning the interdiffusion between indium and antimony will be presented.

Sample Group	Substrate	Deposition Scheme	In:Sb Mass Ratio
А	Glass	8 Layers	0.491g:0.519g (1.00:1.06)
D4	Glass	8 Layers	0.476g:0.505g (1.00:1.06)
F	Glass	3 Layers	0.295g:0.300g (1.00:1.02)
G	Glass	3 Layers	2.05g:2.10g (1.00:1.02)
S	p-Si	8 Layers	0.474g:0.504g (1.00:1.06)

Table 4.1. A summary of different deposition conditions.

The above table summarizes the deposition conditions and substrates for the sample groups the results of which are presented in this chapter.

#### 4.2 RESULTS OF OPEN TUBE NITROGEN ANNEALING

Several samples from group A were heat treated by employing the open tube nitrogen annealing scheme (with annealing cycle 1) as described in Chapter 2. The temperatures used were between  $300^{\circ}$ C and  $400^{\circ}$ C. It is interesting to mention that all the films showed a golden-brown color after the 15 minute heat treatment. (All the as-deposited samples on glass and Si substrates had a shining white surface prior to heat treatment.) This suggests that a layer of metallic oxide was formed on the surface. Similar color was observed by Spivak et al for the InSb thin films treated either in air or argon.<sup>9</sup> Spovak et al reported the presence of  $In_2O_3$  phases in the X-ray diffraction results. It is therefore believed that a layer of  $In_2O_3$  was formed during the heat treatment. If high quality InSb thin films are to be obtained, the open tube method is not recommended.

In addition, the conduction types of the InSb thin films were dependent on annealing temperature. For the samples treated below 340°C, p-type conduction was observed. N-type conduction was observed for the samples treated at temperatures close to 400°C,

# 4.3 COMPOSITION ANALYSIS

Elemental composition for five vacuum heat treated (scheme 3,

cycle 1) samples and an as-deposited sample from group A were analyzed by electron probe micro analysis (EPMA). The samples were treated at temperatures between 350°C and 485°C. All the samples after treatment appeared to be n-type. Table 4.2 is a summary of the electron microprobe results. The atomic ratios are normalized such that the corresponding values of In are always 1.0. As shown in the table, there is a net lost of Sb in all the samples after treatment. The composition does not appeared to be a strong function of heat treatment temperature in this temperature range (350°C - 485°C). The average lost of Sb is about 9% when compared to the as deposited sample. Sb has a much higher vapour pressure than In (the difference is about three orders of magnitude). This difference accounts for the loss of Sb.

Table 4.2. A summary of the electron probe micro analysis.

Sample Number	Treatment Temperature ("C)	In:Sb (Normalized Atomic Ratio)
A-6	350	1.00:0.88
A-7	400	1.00:0.90
A-10	405	1.00:0.91
A-8	450	1.00:0.92
A-9	485	1.00:0.89
A-0	as-deposited	1.00:0.99

#### 4.4 THICKNESS ESTIMATION

The actual thicknesses of the as-deposited and treated films were measured by examining the cross sections.

According to the SEM results (which are not shown), the

thicknesses of the D4 samples deposited by the eight layer method were between 1.6  $\mu$ m and 2.0  $\mu$ m; the average thickness of the samples was 1.8  $\mu$ m. No noticeable reduction in the thicknesses was observed after heat treatments. An estimated thickness of 2.2  $\mu$ m was obtained from the model described in Chapter 2 which reflects an average error of 22%.

The thicknesses of the group G samples deposited by the three layer method ranges from 10  $\mu$ m to 13  $\mu$ m. The average thickness was 11.5  $\mu$ m and the corresponding estimated thickness was 9.3  $\mu$ m. The average error induced was about 24%.

Thus, the model described in Chapter 2 can give a reasonable estimation of the film thickness with an average error of less than 25% for both the three layer and eight layer methods.

#### 4.5 THE GROUP D4 SAMPLES

All the samples in this group were heat treated in vacuum (scheme 3). Annealing cycle 1 was employed. The effects of heat treatment temperature on crystallinity, surface morphology and electrical properties were studied. Results of the magnetoresistance effect measurements will be presented in a later section.

## 4.5.1 X-ray diffraction results

In order to determine the crystalline quality of the treated InSb films, samples were examined by X-ray diffraction. As a reference, the standard ASTM data for InSb crystallized in a cubic

and tetragonal structure is plotted in Figure 4.1. The plots of relative X-ray diffraction intensity versus 20 for three InSb samples treated at different temperatures are shown in Figures 4.2, 4.3, and 4.4. All the samples have a polycrystalline cubic structure.

Sample D4-1, Figure 4.2, which was treated at 530°C (the melting point of InSb is 525°C) has a predominant phase with a preferred (111) orientation. The second and third highest peaks are due to InSb (311) and In (101) respectively. The appearance of the In peak may be because of the loss of Sb during the heat treatment. In fact, when some samples were treated at 540°C, severe vaporization of deposited materials (both In and Sb) was observed. The result of the film (D4-4) treated at 500°C (below the melting point of InSb) is shown in Figure 4.3. The InSb (111) peak is still dominant but the InSb (311) peak is suppressed. The In (101) peak still exists. The result obtained for sample D4-13, treated at 440°C, is shown in Figure 4.4. A more random structure was observed. The highest peak is due to the InSb (111) plane. The second and third highest peaks are due to the InSb (220) and the InSb (311) planes, respectively. Observable peaks due to InSb (331), (422), (400), and (511) planes are also found.

On the whole, polycrystalline films were formed. Highly oriented films with a preferred (111) orientation can be produced by treating the films at temperatures close to the melting point of InSb. For low temperature treatments, the films show a more random structure.

# 4.5.2 Surface morphology

In order to study the change in surface morphology of the InSb thin films, optical micrographs for several samples were taken (with same magnification). A picture of an as-deposited film is presented in Figure 4.5. In the picture, one can clearly see a texture surface. Figure 4.6 shows a picture of the sample treated at 480°C. The film in Figure 4.6 has a different morphology from the as-deposited sample in Figure 4.5. The morphology of the samples treated at temperatures between 410°C and 480°C appeared to be the same. However, as the treatment temperature was increased from 480°C to 530°C, a continuous change in morphology was observed (see Figures 4.7 to 4.10). This result suggests that there was a threshold temperature effect. Once the treatment temperature exceeded 480°C, the reaction between In and Sb became more vigorous.

# 4.5.3 Conduction type

N-type conduction was observed in all the films treated at temperatures between 400°C and 530°C. The results were determined by the methods described in chapter 3.

# 4.5.4 Room temperature conductivity

Room temperature conductivities were obtained by using the method described in chapter 3. Figure 4.11 shows the variation of the room temperature conductivity with the annealing temperature. The conductivity is maximum  $(6.2 \times 10^2 \ \Omega^{-1} \text{cm}^{-1})$  for the film treated

at 530°C and is minimum  $(8.9 \ \Omega^{-1} \text{cm}^{-1})$  for the film treated at 470°C. The conductivities of the films treated at temperatures between 490°C and 530°C are one order of magnitude higher than those of the films treated at temperatures between 400°C and 460°C. The X-ray diffraction results for the samples treated at high temperatures suggest that conductivity is affected by crystalline structure. The highly oriented films have conductivities greater than those of the randomly oriented ones.

# 4.5.5 Hall effect measurements

Electron mobilities (Hall mobilities), electron concentrations, and Hall coefficients were determined using Hall effect measurements mentioned in Chapter 3. Table 4.3 (page 65) summarizes the results obtained from the Hall effect measurements.

Figure 4.12 is a graph of the room temperature Hall mobility versus annealing temperature for several samples. The electron mobility reaches its maximum value of 1.8:10' cm'/V-s for the film treated at 520°C. The lowest mobility is about 90 cm'/V-s for the film treated at 420°C. When the annealing temperature is decreased from 490°C to 450°C, the mobility decreases by one order of magnitude. This is consistent with the results obtained by X-ray diffraction. The highly oriented InSb films have higher electron mobilities and the randomly oriented InSb films have much lower electron mobilities. In addition, a relation was also found between mobility and conductivity. The higher the mobility, the higher the conductivity.

The Hall mobilities obtained for the samples treated at temperatures between 500°C and 520°C are comparable to the value acquired by Nadkarni et al under similar magnetic field.<sup>17</sup> The electron mobilities obtained are still inferior to the value obtained by Okimura et al.<sup>24</sup> In addition, for some of the samples, Hall mobilities were measured at 77°K (see Table 4.3 in page 65). All the mobilities at 77°K were less than the mobilities at room temperature. An average reduction in mobility of 40% was observed. This reduction in mobility implies there is high defect density in these samples. Furthermore, the low room temperature mobility might be due to the unoptimized annealing procedure used and the inhomogeneous nature of the film.

Figures 4.13 and 4.14 display the graphs of room temperature electron concentration versus annealing temperature and Hall coefficient versus annealing temperature, respectively. No particular trend was observed. The electron concentration ranges from  $5.8 \times 10^{10}$  cm<sup>-3</sup> to  $3.5 \times 10^{18}$  cm<sup>-3</sup>. The sample with the highest electron concentration (treated at 420°C) has the lowest mobility. The samples with electron low concentration (treated at temperatures between 500°C and 520°C) correspond to those with high mobility. The Hall coefficient ranges between 2.1 cm<sup>3</sup>/c and 127.8 cm<sup>3</sup>/c. The sample with the highest electron concentration (treated at 420°C) has the lowest Hall coefficient. The samples with low electron concentration correspond to those with high Hall coefficient.

# 4.5.6 Temperature dependence of conductivity

In order to study the effect of annealing temperature on temperature dependent conductivity, two samples, one treated at a higher temperature of 530°C and the other sample treated at 440°C, were examined. The data was obtained for a temperature range between  $80^{\circ}$ K and  $300^{\circ}$ K. The temperature dependence of electrical conductivity ( $\sigma$ ) in the two films is plotted in Figure 4.15.

Due to high electron concentration, the conductivity of the InSb films is larger than that of bulk crystal in the entire measured temperature range.<sup>1</sup> The conductivity curve of the sample treated at 440°C is below the one treated at 520°C. This is due to lower electron mobility. The 300°K conductivity of the film treated at 520°C is about one order of magnitude higher than the corresponding 80°K value. The difference of conductivity for the sample treated at 440°C is only about half an order of magnitude for the same temperature range.

# 4.5.7 Results of 77°K Hall effect measurements

77°K Hall effect measurements were carried out on most of the samples treated at high temperatures. For samples treated at low temperatures, it is difficult to obtain reliable results. This is probably due to the random nature of the films associated with extremely low carrier mobility and high carrier concentration.

As shown in Table 4.3 (page 65), all the measured 77"K mobilities were lower than the corresponding room temperature values. An average mobility reduction of 40% was observed.

Furthermore, the effect of carrier freeze-out is not significant with an average reduction of 28% in carrier concentration. The deviation of the electrical properties from the single crystal specimens can be accounted for by the high defect density, since the films are, at most, polycrystalline.

## 4.6 RESULTS OF X-RAY DIFFRACTION AND SURFACE MORPHOLOGY FOR Insb THIN FILMS DEPOSITED ON (111) ORIENTED SI WAFER

films used for the X-ray diffraction studies were The deposited by the eight layer method. Figures 4.16 and 4.17 show the X-ray diffraction results for two samples. The heat treatment was done by employing the vacuum annealing scheme with temperature cycle 1. The corresponding annealing temperatures were 490°C and 540°C. For the sample treated at 490°C, a more random structure similar to that of sample D4-12 was observed. However, two additional planes were found (InSb (200) and InSb (101)). These two planes belong to the tetragonal symmetry InSb crystals. This indicates that InSb crystallized with a structure which is a mixture of cubic and tetragonal symmetries. The formation of these two phases is likely the result of the interface dislocation associated with the lattice mismatch between single crystal Si and InSb thin film. Hence, the lattice mismatch between Si and InSb is greater than 10%. Furthermore, for the sample treated at 540°C, InSb (111) became predominant. Therefore, similar to the results obtained from the films deposited on glass substrates, highly oriented films can be obtained by treating the films in the high temperature range. The adhesion between the InSb thin film and Si

was found to be better, as a result of higher sticking coefficient or higher binding energy. This can be substantiated by the fact that vaporization of deposited materials observed was negligible for the films treated at temperatures as high as 540°C. Severe vaporization was observed for the films deposited on glass substrates at the same temperatures.

In Figures 4.18, 4.19 and 4.20, the surface morphologies for the films treated at 510°C, 530°C and 550°C respectively are revealed. A continuous change of morphology was observed. However, for the films treated at temperatures between 490°C and 510°C, the surface morphologies appear to be the same. A threshold temperature of 510°C was observed. Below this temperature, the physical reaction between In and Sb is less vigorous. It is interesting to mention that this threshold temperature is 30°C higher than the corresponding value for glass substrates.

Furthermore, all the films deposited on Si substrates were found by the hot probe method to be n-type.

# 4.7 InSb THIN FILMS PREPARED BY THE 3-LAYER DEPOSITION METHOD

Two groups of samples (F and G) were deposited by the three layer method. Group F samples are relatively thin with a thickness of about 1.4  $\mu$ m. Two samples from this group were treated by employing the vacuum tube scheme. Samples F-1 and F-2 were treated using temperature cycles 1 and 2 respectively. N-type conduction was observed in both samples. Table 4.4 shows the corresponding room temperature electrical characteristics.

Sample no.	σ (Ω <sup>-+</sup> -cm <sup>-1</sup> )	μ (cm'/V-sec)	n (cm <sup>-</sup> ')	R <sub>H</sub> (cm`/C)
F-1	62	2.8x10 <sup>4</sup>	1.4x10 <sup>17</sup>	45
F-2	121	2.7x10-	2.8%1017	22

Table 4.4. Electrical properties of group F samples.

The above results showed that the effect of different temperature cycles on the electron mobility is negligible. When the results of the group F samples deposited by the three layer method are compared with the results of the group D4 samples which were deposited by the eight layer method, group F samples have lower electron mobility and higher carrier concentration. This suggests that the eight layer method provides a more complete reaction between the In and Sb layers than the three layer method. This may be because the elemental layers deposited are thinner when the eight layer method is used.

In addition, samples F-1 and F-2 has different surface morphologies. Figure 4.21 is an optical micrograph of sample F-1 which was treated by using temperature cycle 1. The inhomogeneous surface is easily discerned. A more homogeneous surface may be distinguished in sample F-2 which was treated by using temperature cycle 2 (see Figure 4.22). The difference may be attributable to the slow heating and slow cooling properties of temperature cycle 2.

In order to understand the interdiffusion and the growth of InSb thin films. A group of relatively thick films were deposited

(group G). The average thickness was about 11.5  $\mu$ m. The electrical properties of sample G-1, which was treated in a vacuum tube by using temperature cycle 2, are summarized in Table 4.5. An n-type conduction was observed.

Tabl	le 4	4.5.	Electrical	properties	of	sample	G-1.
------	------	------	------------	------------	----	--------	------

Sample no.	$\sigma$	μ	n	R <sub>11</sub>
	$(\mathbf{Q}^{-1}-\mathbf{C}\mathbf{m}^{-1})$	(cm′/V-sec)	(cm <sup>-</sup> `)	(cm'/C)
G-1	71	6.5x10 <sup>°</sup>	6.8x10 <sup>1</sup>	92

The electron mobility obtained in the thick sample is much higher than the mobility in the thin samples deposited by the same method. This increase of the carrier mobility can be emplained by lower electron concentration, less surface scattering and larger crystal grain sizes associated with the larger thicknesses. Figure 4.23 is an optical micrograph showing the surface of sample G-1. In the picture, crystal grains with an average grain diameter of about 7 µm are notable. These were not observed in the thinner group F samples.

In addition, two samples taken from group F and group G, respectively, were treated using the ampoule scheme with temperature cycle 2. Severe segregation was marked. The ampoule heat treatment scheme is therefore not recommended.

# 4.8 MAGNETORESISTANCE EFFECT MEASUREMENTS

Magnetoresistance effect measurements have been carried out on nine samples from groups D4, F and G. Table 4.6 summarizes the

66). results (see page In the table, the change in magnetoresistance is represented as a percentage. There are two columns of change in magnetoresistance values which correspond to  $\beta = 0^{\circ}$  and  $\beta = 90^{\circ}$  (please see Figure 3.10 for the corresponding setup). The large differences between the values in these two columns indicates an anisotropic effect of conduction in the presence of a magnetic field. Indeed, early studies have shown that substances with cubic symmetry (such as InSb and InAs) which behave as isotropic solids in the absence of a magnetic field can show a marked anisotropy when a field is applied.<sup>39</sup> This anisotropic effect has been observed in single crystal InSb.<sup>39</sup>

Generally speaking, if we assume lattice scattering to be the scattering mechanism dominant in the solid and isotropic conduction, а theoretical equation linking the transverse magnetoresistance effect with carrier mobility and applied magnetic field can be developed<sup>19</sup>

$$\sigma = \sigma_0 \left[ 1 - \mu^2 B^2 \left( \frac{8}{\pi} - 2 \right) \right] \qquad \dots \dots (4.1)$$

where  $\boldsymbol{\sigma}$  and  $\boldsymbol{\sigma}_{o}$  are the conductance in the presence and absence of a magnetic field respectively,  $\mu$  is the carrier mobility, and *B* is the applied magnetic field. This equation is valid only for small magnetic fields. For a large magnetic field (e.g. > 1 Tesla), other high field effects are likely to affect the conduction mechanism. The above equation will not be valid.

Thus, by re-arranging the above equation, the change in magnetoresistance can be represented by equation (4.2).

$$\frac{\Delta R}{R_o} = \frac{\mu^2 B^2 \left(\frac{8}{\pi} - 2\right)}{1 - \mu^2 B^2 \left(\frac{8}{\pi} - 2\right)} \qquad \dots \dots (4.2)$$

In the equation,  $\Delta R$  is the change in resistance when a magnetic field is applied and R<sub>o</sub> is the resistance in the absence of a magnetic field. Therefore, for a given magnetic field, a theoretical graph of the change in magnetoresistance can be plotted as a function of carrier mobility. In our case, the magnetic field is about 0.17 Tesla. In Figure 4.24, the theoretical curve is shown (solid line). There are two sets of data points which represent the change in magnetoresistance for  $\beta=0^{\circ}$  (O) and  $\beta=90^{\circ}$  (P). As shown in the figure, the data points can be roughly fitted by the theoretical curve. This verifies the assumption of lattice scattering. In fact, lattice scattering is a common scattering mechanism presented in cubic structure solids such as InSb.

The current dependent magnetoresistance effect has been measured for two samples (F-2 and G-1). Figure 4.25 shows the change in magnetoresistance as a function of current. Both samples demonstrate an essentially constant  $\Delta R/R_o$  over a current range of 0.1 mΑ to 6 mA. Figure 4.26 is а plot of change ın magnetoresistance versus incident angle of transverse magnetic field for sample G-1. A monotonic decrease in  $\Delta R/R_{c}$  is observed as  $\boldsymbol{\beta}$  is increased from 0° to 90°. This demonstrates that anisotropic behaviour varies continuously with the incident angle of the transverse magnetic field.

#### 4.9 STUDY OF THE INTERDIFFUSION BETWEEN IN AND Sb

In order to understand the interdiffusion between In and Sb, several group G samples were treated by employing vacuum annealing scheme with temperature cycle 2. The samples were removed from the furnace at different times, before the cycle was finished.

Figure 4.27 shows an optical micrograph of sample G-2 which was removed once the temperature of the furnace was increased to about 300°C. From the figure, we can see that crystal grain density is small. This indicates that the interdiffusion between the In and Sb layers has just finished. Crystal grain growth has started. Figure 4.28 is an optical micrograph of sample G-3. This sample was retrieved from the furnace when the temperature had just reached 500"C. The density of the grains is much higher in this sample. The sizes of the grains, however, are not uniform. It can therefore be concluded that the formation of crystal grains took place at temperatures higher than 300°C. Figure 4.23 is an optical micrograph of sample G-1 which was retrieved after the annealing cycle was finished. As described before, in Section 4.7, the grain size of this sample was more uniform.

In addition, cross sections of the as-deposited and two of the above mentioned samples were examined by SEM. Figure 4.29 is an SEM picture of the as-deposited sample. Although it has a three layer structure, the first layer is too thin to be observed. For this reason, only two layers are seen in Figure 4.29. The top layer is In and the bottom layer is Sb. The interface between the two layers can be clearly seen. Figure 4.30 is the SEM picture of sample G-2.
There is no clear separation between two layers due to the interfiffusion. Figure 4.31 shows the cross section of sample G-3. A uniform layer is shown, indicating the complete reaction between In and Sb.

In conclusion, the combination of the optical micrograph and SEM pictures allow us to understand physically the interdiffusion between In and Sb at different points of the annealing cycle.

Sample	Annealing	$\sigma$ (Q <sup>-1</sup> cm <sup>-1</sup> )		$\mu$ (cm <sup>2</sup> /V-sec)		n $(x10^{16} \text{ cm}^{-3})$		$B \left( cm^{3}/c \right)$	
no.	Temp. (°C)	300°K	77°K	300°K	77°K	300°K	77°K	300°K	77°K
			-						
D4-1	530	620	-	8400	-	55	48	12 5	15 2
D4-2	520	230	100	18000	12000	9.3	6.2	78.8	119.0
D4-3	510	120	39	15000	7000	5.8	4.1	127 8	10.0
D4-4	500	200	93	16000	9300	9.2	7.4	80 1	100.7
D4-5	490	190	67	11000	7300	12	6.7	60 1	33.7 109.6
D4-7	480	40	-	850	-	35	-	21 2	105.0
D4-10	470	8.9	-	-	-	-	_	21.2	-
D4-11	460	15	-	-	-	_	-	_	-
D <b>4-</b> 12	450	16	3.7	1300	-	9 0	_	01 5	-
D4-13	440	18	_	670	-	19	_	20.5	-
D4-14	430	20	-	-	_	-	_	30.3	-
D4-15	420	41	-	90	_	350	_	-	-
D4-16	410	28	-	-	_	-	-	2.1	-
D4-17	400	24	_	-	-	_	-	-	-
						-	-	-	-

# Table 4.3. Summary of the Hall effect measurements.

Sample Number	μ (cm²/V-sec)	<b>Δ</b> R/R <sub>o</sub> ( <b>β</b> =0°)	$\Delta R/R_{o}$ ( $\beta = 90^{\circ}$ )
D4-2	$1.8 \times 10^{4}$	98	28
D4-3	1.5x104	12%	38
D4-4	1.6x104	78	1%
D4-7	8.5x10 <sup>2</sup>	0.5%	
D4-12	1.3x10 <sup>3</sup>	0.18	_
D4-15	90	0.1%	-
F-1	2.8x10 <sup>3</sup>	0.5%	0.2%
F-2	2.7x10 <sup>3</sup>	1.48	0.78
G-1	6.5x10 <sup>3</sup>	28	1.48

Table 4.6. A summary of the magnetoresistance effect measurements.

.



**Relative Intensity** 

Fig. 4.1. The plot of standard ASTM data as a function of 20 for InSb.



Fig. 4.2. Relative X-ray diffraction intensity versus 20 for a film (D4-1) treated at 530°C, showing peaks corresponding to the cubic structure.



Fig. 4.3. Relative X-ray diffraction intensity versus 20 for a film (D4-4) treated at 500°C.



•

Fig. 4.4. Relative X-ray diffraction intensity versus 20 for a film (D4-13) treated at 440°C.



Fig. 4.5. An optical micrograph of an as-deposited film. The vertical bar represents 50  $\mu m.$ 



Fig. 4.6. An optical micrograph of a film treated at 480°C. The vertical bar represents 50 µm.



Fig. 4.7. An optical micrograph of a film treated at 490°C. The vertical bar represents 50  $\mu m$  .



Fig. 4.8. An optical micrograph of a film treated at 500°C. The vertical bar represents 50  $\mu m$  .



Fig. 4.9. An optical micrograph of a film treated at 520°C. The vertical bar represents 50  $\mu m.$ 



Fig. 4.10. An optical micrograph of a film treated at 530°C. The vertical bar represents 50  $\mu m.$ 



Fig. 4.11. Room temperature conductivity versus annealing temperature of the evaporated InSb films (group D4).



Fig 4.12. Room temperature Hall mobility as a function of annealing temperature for D4 samples.



Fig 4.13. A graph of room temperature electron concentration versus annealing temperature for D4 samples.



Fig 4.14. A plot of Hall coefficient as a function of annealing temperature for D4 samples.



Fig. 4.15. Temperature dependent conductivity curve for samples treated at 520°C (D4-2) and 440°C (D4-13).



Fig. 4.16. X-ray diffraction result for a sample deposited on Si wafer and treated at 490°C.



~

Fig. 4.17. X-ray diffraction result for a sample deposited on Si wafer and treated at 540°C.

.



Fig. 4.18. An optical micrograph of a film deposited on Si substrate and treated at 510°C. The vertical bar represents 50 µm.



Fig. 4.19. An optical micrograph of a film deposited on Si substrate and treated at 530°C. The vertical bar represents 50 µm.



Fig. 4.20. An optical micrograph of a film deposited on Si substrate and treated at 550°C. The vertical bar represents 50  $\mu m.$ 



Fig. 4.21. An optical micrograph of sample F-1. The vertical bar represents 50  $\mu$ m.



Fig. 4.22. An optical micrograph of sample F-2. The vertical bar represents 50  $\mu$ m.



Fig. 4.23. An optical micrograph of sample G-1. The vertical bar represents 30  $\mu m.$ 



Fig. 4.24.

Theoretical results.



Fig. 4.25.  $\Delta R/R_{\circ}$  plotted as a function of current for samples F-2 and G-1.



Fig. 4.26. The results of the angle dependent magnetoresistance effect for sample G-1.

Se .



Fig. 4.27. An optical micrograph of sample G-2. The vertical bar represents  $50 \ \mu m$ .



Fig. 4.28. An optical micrograph of sample G-3. The vertical bar represents  $50 \ \mu\text{m}$ .



Fig. 4.29. A SEM picture of an as-deposited sample.



Fig. 4.30. A SEM picture of sample G-2.



Fig. 4.31. A SEM picture of sample G-3.

## Chapter 5 CONCLUSIONS

Thin films of InSb have been prepared on glass and (111) oriented single crystal Si substrates successfully. The films were prepared by multilayer vacuum deposition followed by heat treatment under different conditions. The electrical and physical properties of the InSb thin films were studied by the various methods described in Chapter 3. From the results presented in Chapter 4, some important conclusions may be drawn. The conclusions are summarized below.

- (1) Open tube nitrogen and ampoule heat treatment schemes are not recommended. The best results are obtained by employing vacuum tube heat treatment.
- (2) Composition analysis revealed that there was a net lost of Sb following the heat treatments in vacuum.
- (3) The mathematical model discussed in Chapter 2 is capable of estimating the thickness of the deposited films with an error of less than 25%. From the SEM results, no noticeable reduction in thickness was observed after the heat treatments in vacuum.
- (4) Results of X-ray diffraction showed that vacuum treated InSb thin films prepared on glass substrates have a polycrystalline cubic structure. The films treated at temperatures above 490°C were highly oriented with a preferred (111) orientation. The

films treated at temperatures of several tens of degrees above 400°C had more random structures.

- (5) InSb thin films prepared on Si substrates had a mixed cubic and tetragonal structures when treated at temperatures between 490°C and 550°C. A (111) preferred orientation was found for the films treated at around 540°C.
- (6) A threshold temperature of 480°C and 510°C was found for the films prepared on glass and Si substrates, respectively, by examining the surface morphologies. Below the threshold temperatures, surface morphologies did not change with treatment temperature. A continuous change in morphologies with treatment temperature was observed when treatment temperatures were higher than the corresponding threshold values.
- (7) InSb thin films prepared on Si substrates had better adhesion than films prepared on glass substrates which experienced severe vaporization at treatment temperatures higher than 530°C. The vaporization in films deposited on Si substrates was negligible at treatment temperatures as high as 540°C.
- (8) An n-type conduction was found for all the vacuum treated samples.
- (9) The electrical conductivity of the InSb thin films was found to be affected by the crystalline structure. The more ordered the structure, the higher the conductivity. Room temperature conductivity decreased by one order of magnitude when the annealing temperature was decreased from 490°C to 460°C.

- (10) From room temperature Hall effect measurements, it was found that carrier mobility increased as conductivity increased. A mobility as large as 1.8x10<sup>4</sup> cm<sup>2</sup>/V-sec was observed in a film treated at 520°C.
- (11) An average mobility reduction of about 40% from the 77°K Hall effect measurements was observed when the temperature was decreased from 300°K to 77°K. The effect of carrier freeze-out is not significant in this temperature range. The average reduction was 28%.
- (12) Generally speaking, the values of mobility for the films deposited by the three layer method were lower than the corresponding values for the films deposited by the eight layer method. It is believed that thinner elemental layers can improve film quality.
- (13) There was not much difference in the electrical properties between the films treated using temperature cycles 1 and the films treated using temperature cycle 2. Temperature cycle 2 does yield a more homogeneous morphology. This homogeneous morphology is believed to be the result of the slow cooling and heating procedures.
- (14) Crystal grains with an average diameter of about 7 µm were observed in the InSb films, with an average thickness of 11.5 µm, treated by using temperature cycle 2.
- (15) Anisotropic conduction was observed in the presence of a small magnetic field from the transverse magnetoresistance effect measurements. The experimental results can be fitted by the

theoretical curve if lattice scattering is assumed.

- (16) The change in magnetoresistance is essentially constant over a current range of 0.1 mA to 6 mA.
- (17) Anistropic behaviour was found to vary continuously with the incident angle of the transverse magnetic field.
- (18) There was interdiffusion between In and Sb at temperatures below 300°C. Above this temperature, the crystal grains start to grow. These findings were ascertained from SEM and optical micrograph studies.

The present investigation shows multilayer deposition followed by vacuum annealing can produce highly oriented polycrystalline InSb thin films. This simple method has potential for large scale industrial purposes. The carrier mobility of the InSb thin films prepared in the present work is still low. More work should therefore be done to optimize the deposition and annealing procedures in order to produce films with higher carrier mobility.

#### Appendix A

### PHOTOLITHOGRAPHY PROCESS

This procedure should be carried out under yellow light condition. Put the sample on the spinning jig of the spinner. 1. 2. Apply 3-5 drops of positive photoresist onto the sample. 3. Spin the sample at 5000 rpm for 15 seconds. 4. Pre-bake at 100°C for 15 minutes. Expose with the mask aligner under UV light for 30 seconds. 5. 6. Develop with the Shipley developer (undiluted) for 1 minute. 7. Rinse with D. I. water. 8. Spin dry the sample Post-bake the wafer at 100°C for 15 minutes. 9. The sample is now ready for the etching step.

#### REFERENCES

- 1. M. Neuberger, Handbook of Electronic Materials Vol. 2: III-V Semiconducting Compounds (IFI/Plenum), pp. 77-92.
- K. F. Hulme and J. B. Mullin, Solid State Electron. 5, 211 (1962).
- T. Sudersena Rao, J. B. Webb, D. C. Houghton, J. M. Baribeau,
  W. T. Moore, and J. P. Noad, Appl. Phys. Lett. 53, 51 (1988).
- 4. R. Rousina and J. B. Webb, Semicond. Sci. Technol. 6, C42 (1991).
- 5. G. Ziegler, Solid-State Electron. 6, 680 (1963).
- 6. J. C. M. Brentano and J. D. Richards, Phys. Rev. 94, 1427 (1954).
- R. F. Potter and H. H. Wieder, Solid-State Electron. 7, 253 (1964).
- H. H. Wieder and A. R. Clawson, Solid-State Electron. 8, 467 (1965).
- 9. J. F. Spivak and J. A. Carroll, J. Appl. Phys. 36, 2321 (1965).
- 10. H. H. Wieder and D. A. Collins, Appl. Phys. Lett. 8, 239 (1966).
- 11. W. J. Williamson, Solid-State Electron. 9, 213 (1966).
- 12. H. H. Wieder, Solid-State Electron. 9, 373 (1966).
- 13. J. A. Caroll and J. F. Spivak, Solid-State Electron. 9, 383 (1966).
- 14. A. R. Clawson and H. H. Wieder, Solid-State Electron. 10, 57 (1967).
- 15. N. F. Teede, Solid-State Electron. 10, 1069 (1967).
- 16. H. H. Wieder and D. A. Collins, Solid-State Electron. 11, 1093 (1968).
- 17. G. S. Nadkarni, A. Simoni, and J. G. Simmons, Solid-State Electron. 18, 393 (1975).

- 18. M. Isai and M. Oshita, J. Appl. Phys. 55, 941 (1984).
- 19. M. Isai and M. Oshita, J. Appl. Phys. 58, 2686 (1985).
- 20. M. Isai, T. Fukunaka, and M. Oshita, J. Appl. Phys. **59**, 2845 (1986).
- 21. M. Isai and M. Oshita, J. Appl. Phys. 65, 391 (1989).
- 22. S. Iida, J. Appl. Phys. 65, 636 (1989).
- 23. S. Iida, J. Appl. Phys. 65, 1977 (1989).
- 24. H. Okimura, T. Matsumae, and M. Oshita, J. Appl. Phys. 66, 4252 (1989).
- 25. S. Kaur and R. K. Bedi, Mat. Res. Bull., 25, 1421 (1990).
- 26. M. Isai, J. Beerens, and J. D. N. Cheeke, J. Appl. Phys. **69**, 7130 (1991).
- 27. A. J. Bosch, R. G. van Welzenis, and O. F. Z. Schannen, J. Appl. Phys. 58, 3434 (1985).
- 28. G. M. Williams, C. R. Whitehouse, C. F. McConville, A. G. Cullis, T. Ashley, S. J. Courtney, and C. T. Elloitt, Appl. Phys. Lett. 53, 1189 (1988).
- 29. T. Ashley, A. B. Dean, C. T. Elliott, C. F. McConville, and C.R. Whitehouse, Electronics Letters 24, 1270 (1988).
- 30. J.-I. Chyi, D. Biswas, S. V. Lyer, N. S. Kumar, and H. Morkoc, Appl. Phys. Lett. 54, 1016 (1989).
- 31. K. D. Jamison, A. Bensaoula, Ignatiev, C. F. Huang, and W. S. Chan, Appl. Phys. Lett. 54, 1916 (1989).
- 32. P. E. Thompson, J. L. Davis, J. Waterman, R. J. Wagner, D. Gammon, D. K. Gaskill, and R. Stahlbush, J. Appl. Phys. 69, 7166 (1991).
- 33. G. E. Franklin, D. H. Rich, H. Hong, T. Miller, and T.-C. Chiang, Physical Review B 45, 3426 (1992).
- 34. J. C. Chen, P. Bush, W. K. Chen, and P.-L. Lin, Appl. Phys. Lett. 53, 773 (1988).
- 35. M. Pirani and J. Yarwood, Principles of Vacuum Engineering (Chapman and Hall, London, 1961), pp. 314-316.

- 36. L. Ward and J. P. Bunn, Introduction to the Theory and Practice of High Vacuum Technology (Butterworths, London, 1967), p. 5.
- 37. L. Eckerlova, Physics of Thin Films (Plenum Press, 1977).
- 38. A. Segmuller and M. Murakami, Thin Films from Free Atoms and Particles, (Academic Press, 1985), Chapter 8.
- 39. E. H. Putley, The Hall Effect and Related Phenomena (Butterworths, London, 1960).
- 40. S. M. Sze, Physics of Semiconductor Devices (John, Wiley & Sons, 1981).
- 41. R. F. Pierret, Modular Series on Solid State Devices, Volume I: Semiconductor Fundamentals, 2nd edition (Addison Wesley, 1988).
- 42. Scanning Electron Microscopy, X-Ray Microanalysis, and Analytical Electron Microscopy, A Laboratory Workbook (Plenum Press, 1990).
- 43. R. Theison, Quantitative Electron Microprobe Analysis (Springer-Verlag, 1965).