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

PREPARATION AND INVESTIGATION OF DOPED ZnO FILMS

by

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Transparent low resistivity ZnO films with a typical thickness of 1 micron have been deposited on glass substrates by an rf magnetron sputtering method. The $2n\sigma^{\prime}$ films were polycrystalline with a (002) preferred orientation. It was found that both the electrical and optical properties of the films were affected by adding In203 or Al203 as sources of dopant. For the In-doped films, the resistivity of the central region was observed to decrease by three orders of magnitude as In₂O₂ content increased from 0 to 5.3 wt%. A similar effect was observed for the Al-doped films. It was also found that the film resistivity varied with substrate position. For the films deposited on vertical substrates, the resistivity was lower than that of horizontal ones deposited under the same conditions. Furthermore, it was found that the resistivity of ZnO films deposited on the horizontal substrates varied with distance from the target center. From Hall effect measurements, this resistivity variation was shown to be due to a variation of carrier mobility along the substrates.

ABSTRACT

In the present work, thermal stability of the ZnO films in air was confirmed to improve by the doping. For the undoped ZnO films, the resistivity increased by about 3 orders of magnitude after an air heat treatment at 250°C. For the heavily doped ones, however, the resistivity remained essentially constant after similar treatment. For the films deposited on vertical substrates, the resistivity was found to be not as stable as the

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films deposited on horizontal substrates. In addition, the thermal stability of ZnO films was observed to be affected by the treatment temperatures. The resistivity values increased drastically with time at high temperature (for example 350°C). This increase was believed to be due to diffusion of oxygen. For the films doped with Al or In, the carrier mobility was observed to decrease during the air treatment. A decrease in carrier concentration with the treatment time was found for the In-doped films. For those doped with Al, the carrier concentration remained roughly constant during the air treatment. For the air treatment under 250°C, the resistivity of doped films remains constant. The present results thus suggested that the doped ZnO films can be used for photovoltaic device fabrication.

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RESUME

Des films transparents de OZn, de faible résistivité et d'épaisseur tipique 1 micron ont été déposés sur des substrats en verre par pulvérisation, en utilisant un magnétron rf.

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Les films étaient polycrystallins, orientés préférentiellment suivant la direction (002). Il a été trouvé que l'addition des sources de dopants In_2O_3 et Al_2O_3 influençaient à la fois les propriétés électriques et optiques des films. Pour les films dopés à l'In, on a observé que la résistivité de la région centrale diminue de 3 ordre de grandeur lorsque la concentration au In_2O_3 augmente de 0 à 5.3 masse %. Un effet similaire a été observé pour les films dopés à l'Al. On a aussi remarqué que la résistivité du film varie avec la position du substrat: la résistivité des films déposés sur des substrats verticaux était plus faible que celle de ceux, déposés dans les mêmes conditions, sur des substrats horizontaux. De plus, on a trouvé que la résistivité des films de OZn déposés sur des substrats horizontaux varie avec la distance au centre de la cible. Des mesures par effet Hall ont permis de montrer que la variation de la résistivité est due à une variation de la mobilité des porteurs le long du substrat.

Le travail présenté ici confirme que la stabilité thermique des films de OZn s'améliore avec le dopage. Pour des films non dopés, la résistivité augmentait d'environ 3 ordre de grandeur à la suite d'un traitement thermique à l'air, à 250°C. En revanche, dans le cas de films très dopés, la résistivité restait pratiquement constante après un traitement similaire. Quant aux films déposés sur des substrats verticaux, on a trouvé que leur resistivité n'est pas aussi stable que celle de ceux déposés sur des substrats horizontaux. De plus, il a été observé que la stabilité thermique des films de OZn est affectée par la température de traitement.

La valeur de la résistivité augmentait dramatiquement en fonction du temps à haute température (à 350°C par exemple). Cette augmentation est présumément due à une diffusion d'oxygène. Pour des films dopés à Al ou In, la mobilité des porteurs s'est avérée décroître pendant le traitement à l'air. Une diminution de la concentration des porteurs en fonction de la longueur du traitement a été observée pour les films dopés à In. Pour aux dopés à Al, la concentration des porteurs restait approximativement constante pendant le traitement. D'autre part, dans le cas de traitement thermique à l'air à des températures inférieures à 250°C, la résistivité des films dopés reste constante.

De tels résultats on suggeré la possibilité d'utiliser les films de ZnO dopés pour la fabrication de dispositifs photovoltaiques.

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IV

, (C

	۲			
	IJ			
		•	TABLE OF CONTENTS	ł
	,	۰.	e en f	Page
-				
ن ک ر.	ABSTRACT	' J		I
	DECIME	. 1		
	RESUME			***
	ACKNOWLE	DGEMENT	₩	, İv
	TABLE OF	CONTEN	TS ;	v
	СНАРТЕВ	'n		1 [,]
	Survey and the second s	•		•
	CHAPTER	Ž	RF SPUTTERING SYSTEM AND FILM DEPOSITION	6
	,	-in a	· · · ·	•
ت		* 2.1 2.2	Introduction	-6 "
		4.2	System	6
		2.3	Film Deposition	Ű 10
	ę	2.3.1	Target Preparation	10
		2.3.2	Substrate Preparation	11
	*	2.3.3.	Deposition Procedure	11
		2.4 \	Conclusions	13
	. `		· · · · · · · · · · · · · · · · · · ·	
	CHAPTER	3,	FILM CHARACTERIZATION	16
	4 •			٢.
	÷	3.1	Introduction	16 ,
,		3.2	Thickness Measurements	16
		3.3	X-ray Diffraction	19
۰.	•1	3.4	Optical Transmission Measurements	20
	0	3.5	Electrical Resistivity Measurements	21
ø	6	3.6	Hall Effect Measurements	22
			DECRETER OF AC DEDOCTMED 200 ETTMC	25
	CHAPTER •	4	PROPERTIES OF AS-DEPOSITED ZNO FILMS	35 °
`		4.1	Introduction	35
		4.2	Thickness Measurements	35
		4.3	Crystal Structure of ZnO Films	36
-	*	4 4	Ontical Transmission	38
-	ı	4 5	Resistivity	30
		4 5 1	Doning Effect	40
`		4 5 2	Position Effort	40
		4.5.2	Wall Effort	40
	*	4.6 1	Doning Effort	42
		4 6 2	Doping Effect	45
	•	4.0.2	Conclusions	44
		701	Concrustons ,	40
	[•] CHAPTER	5,	EFFECTS OF HEAT TREATMENT ON ZnO FILMS	65
	• ·	-		-
		C 1	Introduction	65 '
		D • 1	Incloadocion	VU
		5.1 5.2	Doping Effect and Air Heat Treatments	66
		5.2 5.3	Doping Effect and Air Heat Treatments Orientation Effect	66 68

Ċ

Ŕ

4

V

5.5 Optical Transmission ' Effect of Different Treatment Gases on, 71 5.6 ZnO Films Effects of Heat Treatment on Carrier Concentration and Mobility Conclusions 72 5.7 75 5.8 76 CHAPTER CONCLUSIONS 6 93 ۱ 97 REFERENCES ŝ

į,

(

¢

CHAPTER 1 INTRODUCTION

The development of new energy resources becomes more and more important since the quantity of the current major energy resources is limited. The renewable energy resources, which include sunlight, ocean current, wave, wind and falling water, can be advantageously used to replace of the current major energy resources. For these energy resources, sunlight or solar energy is the most attractive one. The magnitude of solar energy falling on the earth is about 7.45×10^{17} kWh annually while the present consumption of the world is only about 0.5×10^{14} kWh annually [1.1].

The current major problem for the application of the solar energy is the development of a low cost procedure for high efficiency solar cells. These cells will be used for the direct conversion of solar energy into electricity, which is very interesting and has been wildly studied currently.

The photovoltaic solar cell basically is a pn junction either in a homojunction or heterojunction form. At the present, the most attractive materials for such applications are CdTe, a-Si and CuInSe₂. This is due to the special optical and electrical properties of these materials. In our laboratory, several projects are being carried out on the semiconductor CuInSe₂, specifically on low cost thin film methods [1.2][1.3][1.4]. Using CuInSe₂ thin films, heterojunction solar cells have been

fabricated and energy conversion' efficiencies of about 12% have been reported[1.5][1.6].

For heterojuction cell fabrication, it is very important to find a suitable window material. The requirements of the window material are as follows: low electrical resistivity, small lattice mismatch with the base material (CuInSe₂), high optical transmission and low cost. Window materials like CdS [1.6][1.7], ITO[1.8], ZnSe[1.9] and $In_2O_3[1.10]$ have been widely studied for such applications.

In the present work, experiments have been made to fabricate and study another interesting window material, ZnO. Comparing with other window materials, ZnO has several advantages.

(1) It has a large energy gap of about 3.3 eV, therefore, most of the photons in the solar spectrum can pass through it.

(2) Films with low resistivity can be achieved.

(3) Low cost of material.

(4) Not toxic.

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The semiconductor ZnO has a direct energy gap and usually shows n-type conduction. For ZnO crystallized in a wurzite form, the lattice parameters are: a=3.249 Å, c=5.205 Å. For a cubic structure, a=4.58 Å. The density of states of the conduction band is about 1×10^{18} cm⁻³. The effective mass is 0.38 (m^{*}/m) for electrons and is 1.8 (m^{*}/m) for holes. The highest mobility reported for electrons in ZnO is 190° cm²V⁻¹sec^{-1^{*}} at room

temperature [1.1].

Low resistivity ZnO thin films can be achieved either by controlling the stoichiometry or by introducing dopants. Research experiments reported in literature on the preparation of low resistivity ZnO films are briefly described below.

Using a reactive evaporation method, Morgan and coworker [4.11] described the deposition of undoped ZnO films in a vacuum chamber containing high purity oxygen. Transparent films with a room temperature resistivity as low as 0.0014 ohm-cm and a carrier concentration of about 10^{20} cm⁻³ have been obtained.

Results also have been reported by Webb and coworkers [1.12][1.13] using a reactive sputtering method. In their experiments, ZnO thin films (resistivity as low as 5×10^{-3} ohm-cm) were deposited on heated substrates from a high purity ZnO target. A mixture of Ar and H₂ was used as the sputtering gas during the experiments to control the conductivity of the ZnO films.

A low cost spray pyrolysis method also has been used for the preparation of ZnO thin films. Using this method [1.14], films with a resistivity of 10^{-3} ohm-cm have been achieved by depositing them on substrates at a temperature of about 400° C followed by a post annealing either in N₂ or H₂.

Using a conventional rf sputtering method, Ito and Nakazawa « [1.15] prepared low resistivity ZnO thin films (5x10⁻³ ohm-cm) on glass substrates. In their experiments, pure Ar was used as the

sputtering gas and high purity ZnO was used as the target.

Recently, Minami and coworkers [1.16][1,17] have produced ZnO thin films with a resistivity as low as 10^{-4} ohm-cm using a modified rf magnetron sputtering method. In their experiments, an external dc magnetic field was applied during the deposition. They found that the carrier mobility of the deposited ZnO films was as high as $100 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$. They also found a positional effect of resistivity of the ZnO films. The resistivity of the samples deposited on substrates held perpendicular to the target surface was observed to be lower than that for the films deposited on substrates placed parallel to the target surface.

The above described experiments were carried out using undoped ZnO materials. For the deposition of low resistivity ZnO films, it is especially interesting to investigate the effect of doping. Minami and coworkers adopted Al (1 to 2wt%) as dopants and found that the resistivity of the ZnO films can be further reduced [1.18][1.19]. However, the carrier mobility of the ZnO films was lower than that of the undoped ones.

From the above brief survey of research experiments on the low resistivity ZnO films, it is clear that there are still several important questions remained to be answered. For example, the thermal stability of the low resistivity ZnO films at elevated temperatures is not known. The thermal stability of the window materials at elevated temperatures is specially important for dewices applications where a post heat treatment is need. It

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is also not clear whether the positional effect observed for the undoped ZnO films is also present in the doped ones.

In present work, an rf.sputtering method has been used to deposit transparent and low resistivity ZnO films. In and Al were used as dopants to achieve the low electrical resistivity [1.20][1.21]. Efforts have been made in order to answer the above described questions.

The arrangement of this thesis is as follows. In chapter 2, the principles of the rf sputtering technique are first introduced, the rf unit used in our laboratory and the procedure for the film deposition are then described. The measurement, techniques used in the present work are presented in chapter 3. In chapter 4, the electrical and optical measurement results obtained for the ZnO films are described in details. The thermal stability study of the ZnO films are then discussed in chapter 5. Finally, in chapter 6, main conclusions of the present work are

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CHAPTER 2 RF SPUTTERING SYSTEM AND FILM DEPOSITION

2.1 Introduction

As described in chapter 1, low resistivity ZnO thin films can be achieved either by controlling the stoichiometry of the films (without impurity) or by doping. For the undoped films, the donor, levels are created by excess Zn atoms or oxygen vacancies. For the doped films, the donor levels are created by the addition of group three elements such as Al, In and Ga.

In the present work, an rf magnetron sputtering method has been used to deposit low resistivity and transparent ZnO thin films. During the deposition, impurities were introduced to the films to reduce the resistivity. The deposition system and the deposition procedure are described in this chapter.

2.2 Principle of Sputtering and RF Sputtering System

Sputtering technique is one of the most effective methods for the fabrication of good quality thin films. The principle of sputtering is based on the fact that when a solid or liquid is bombarded by suitable high energy ions, it is possible for individual atom of the target to get enough energy (from collision with the incident ions) to escape from the target

surface [2.1]. The simplest method of sputtering is the cathode sputtering (or DC sputtering) method. The principle of the cathode sputtering is as follows. The material to be sputtered is used as a cathode in the sputtering system and a glow discharge is formed in an inert gas (e.g. Ar) at a low pressure (10^{-1} to 10^{-2} torr). The positive ions (e.g. Ar⁺) created from the discharge are accelerated by the potential difference between the cathode and the anode and eventually bombard the target. The cathode material is removed by the bombardment and deposited on the anode (substrates).

5

The DC sputtering technique has been extensively studied and used to sputter conductive materials. However, this method can not be used effectively to sputter nonconductive materials because a surface charging effect of the insulators. Therefore, instead of the DC sputtering, an rf sputtering technique has to be used to deposit the nonconductive materials. Different from the cathode sputtering method, the rf power supply is referenced to ground and the rf power can generate plasma and accelerate "ions to the target to cause sputtering.

Compared with the cathode sputtering, the rf sputtering method has two advantages. First, the target is not necessary to be electrically conductive since an rf voltage can be coupled through any kind of impedance. Of course, films also can be sputtered from a conducting target using the rf sputtering system since the target is capacitively coupled to the power

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supply. Furthermore, the secondary electrons can obtain sufficient energy in the glow space to cause an ionizing collision. The creation of secondary electrons is a very important concept in the rf sputtering process. Electrons are accelerated away from the target since a negative voltage is applied to the target. These electrons will help to maintain the glow discharge by ionizing the Ar atoms and when Ar ions bombard the target, more secondary electrons will be generated in an avalahche process. On the other hand, although electnons will lose part of their energy during the collision with Ar ions, they will impinge the substrate eventually with a high enough energy and cause an increase of target temperature.

In order to minimize the effect of secondary electrons on the substrate temperature and to increase the ionization efficiency, an axial magnetic field can be introduced. This magnetic field, which is parallel to the target surface, is formed on top of the target and will force the secondary electrons to follow along a helical path. This helical trajetory will give a longer path to the secondary electrons and therefore increase the probability of ionization collision before these electrons reach the anode and reduce their impinging speed. The magnetron also can be advantageously used to reduce the pressure in the sputtering chamber. The typical pressure during the magnetron sputtering process is in a range from 1 to 10 mtorr, which is about 1 order of magnitude lower than that used in the

DC sputtering system. However, the magnetic field also moves the discharge away from the target centre and causes a nonuniform deposition. Fortunately, in a system with a low field and a small target, this effect will not be very important [2.2].

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In this study, an rf magnetron sputtering system (shown in Fig. 2.1) has been used to deposit low resistivity ZnO thin films. This system includes a Varian vacuum unit and an rf unit. The vacuum unit consists of a 12-inch glass chamber, a 4-inch diffusion pump and a rotary pump. The pressure in the chamber is measured by a thermocouple and an ionization gauges. The diffusion pump with a cold trap and a thermocouple gauge is, isolated form (or connected to) the vacuum chamber by 'a high vacuum valve and a control valve. The rotary pump is isolated from (or connected to) the vacuum chamber by a roughing valve. The rotary pump and diffusion pump are isolated from (or connected to) each other by a foreline valve. A vent valve is used to let air into the vacuum chamber.

The rotary pump can be used to pump the vacuum chamber from atmosphere to a pressure of few ten mtorrs (roughing position) and is also used to maintain a low pressure required for the diffusion pump (foreline position). The diffusion pump is used to pump the vacuum chamber after the chamber has been pumped to about 60 mtorr by the rotary pump. The thermocouple gauge 1 is used to detect the pressure of the chamber when the pressure is more than 10 mtorr. The ionization gauge is used to detect the

f pressure when it is less than 10 mtorr. The thermocouple gauge 2 is used to monitor the pressure of the diffusion pump.

Inside the vacuum chamber, there is an L-shape aluminum sample holder for the glass substrates. There is also an rf gun which is water cooled. The ZnO target is mounted on the top of the rf gun.

The rf gun is connected to the 500 W power supply which is associated with the rf generator and the rf/dc converter (model No. RF5000MB). An rf potential is formed between the target and ground which is used to ionize the Ar atoms and to accelerate Ar ions to bombard the target.

2.3 Film Deposition

The procedure of ZnO thin films deposition includes target preparation, substrate preparation and vacuum deposition.

2.3.1 Target preparation

High purity ZnO powder (59's) and high purity In_2O_3 or Al_2O_3 powder were weighted by using a balance and mixed in a clean beaker for at least 5 min. The mixed powder (about 10 g) was pressed by using a small hammer into an aluminum holder (diameter 4.7 cm) to form a target. The target was then mounted

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on the top of the rf gun. In order to study the effect of doping concentration, ZnO targets containing 0.5, 2, 4 and 5.3wt% In_2O_3 , were prepared for the deposition of ZnO thin films.

2.3.2 Substrate preparation

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Pre-cleaned microscope glass slides from Fisher Scientific with an area of $75x25 \text{ mm}^2$ were used as substrates which were mounted on the L shape Al sample holder. In order to study effects of the substrate position on the properties of ZnO films, glass substrates were placed either perpendicular or parallel to the target surface (as shown in Fig. 2.1). The distance between the target and the horizontal substrate and the lower edge of the vertical substrate is about 4 cm.

2.3.3 Deposition procedute

After the substrates and the target were mounted into the vacuum chamber, the roughing valve was opened and the chamber was pumped by the rotary pump. When the chamber pressure reached a value below 60 mtorr, the roughing valve was closed and the baking valve was opened. Following this, the high vacuum valve was opened and the chamber was pumped by the diffusion pump. The

final pressure of the chamber would reach 10^{-6} torr range after a period of about 2 hours.

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When the pressure of the chamber was pumped down to about 10^{-6} torr, high purity Ar gas was then introduced into the chamber by opening a needle valve. The valve was maintained at a fixed position to keep the chamber pressure at about 20 mtorr for 1 min. The valve was then closed and the pressure of the chamber quickly returned to the high vacuum level. This process was repeated again to minimize the content of air in the copper tube connecting the vacuum chamber and the gas cylinder.

The rf power supply and the rf generator were turned on and a period of about 3 min. was allowed to warm up the filament of the rf tube. When the rf tube was ready, the pressure of the vacuum was then increased to about 10 mtorr by opening the needle valve and the rf power turned on to initiate the plasma. After this, the chamber pressure was controlled to a predetermined value (e.g. 5 mtorr).

During the sputtering process, the incident rf power was controlled to 60 W and the typical deposition time was about 2 , hr. The substrate temperature, which is believed to be important in determining the film quality, increases to about 100° C when incident power is fixed at 85 W [1.17]. Therefore, after each 30 min. of sputtering, the deposition was stopped for 10 min. to let the substrate cool.

After the complete deposition, the rf power was turned off

and the substrates were allowed to cool for at least 15 min. before removing them from the chamber. The samples were then numbered and kept in a plastic box and they were ready for testing.

To minimize the influence of the target surface composition (which was changing with time) during the deposition, a small amount of target raw material was introduced to the surface and was pressed again to form a new target surface after 5° consecutive deposition runs (total time of 10 hr.).

2.4 Conclusions

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Thin films of ZnO have been deposited by using the rf magnetron sputtering method. The rf magnetron sputtering method is a commercially accepted technique for the deposition of thin films especially from nonconductive targets. This is because the relatively low substrate heating, high deposition rate, large area coverage, and low deposition induced damage in the grown films. Using this method, the film thickness can be controlled easily and relatively accurately.

In this project, in order to obtain low resistivity ZnO thin films, weighted amounts of In_2O_3 and Al_2O_3 were introduced into ZnO targets. The typical deposition conditions are as follows: Initial chamber pressure 10^{-6} torr; pressure during

deposition 5 mtorr; weight of the target material 10 g; distance between the target and substrates 4 cm; incident rf power 60 W; deposition time 120 min. In the present work, the glass substrates were placed either parallel or perpendicular to the target surface to investigate how the the properties of the films were affected by the position of the substrates. In order to study the effects of doping concentration, targets with different In_2O_3 contents were also used to deposit the ZnO films.

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Fig. 2.1 RF sputtering system.

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CHAPTER 3 FILM CHARACTERIZATION

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3.1 Introduction

There are several important parameters for the characterization of thin film materials, such as: thickness, compositional uniformity, crystal structure, optical transmission values, electrical resistivity, concentration and mobility of charge carriers. In order to obtain these parameters for the deposited ZnO films, several measurements have been carried out. First of all, film thickness was measured by an optical method. Crystalline quality of the ZnO films was examined by an X-ray diffraction technique. Optical transmission characteristics of the films were also obtained by using a monochromator. Resistivity of the films was measured using a conventional four point probe unit. Carrier concentration and mobility were finally determined by the Van der Pauw method.

In this chapter, the principles and the equipment of the measurements will be described first. The experimental procedure will then be introduced.

3.2 Thickness Measurements

The thickness of the thin films is a very important parameter and must be determined before the determination of other physical parameters. In this project, a very simple optical method has been used to determine the thickness of the ZnO films.

The principle of the optical method is based on interference of light in the thin films. When visible light with a wavelength from 4000 to 8000 Å is incident on the surface of a film, interaction of two or more rays causes the intensity of the light to increase or to decrease in a specific direction [3.1].

As shown in Fig. 3.1, when an incident light reaches the top surface of the thin film, it will be partially reflected and partially refracted. When the refracted light reaches the bottom surface; it is partially reflected to the top surface and is refracted again. For a transparent material, the intensity of the reflected light usually is much lower than the refracted light. Therefore, it is sufficient to consider only the interference of the first two reflected rays.

The difference in the optical path of the interacting light beams is:

 $\Delta 1 = (O\dot{C} + OC_1)n - OF = \frac{2t*n}{\cos\beta} - 2t*tan\beta*sin\alpha \qquad (3.1)$

Here in is the refractive index of the film, and $n = \sin \alpha / \sin \beta$.

 $\Delta 1 = \frac{2t \sin \alpha}{\cos \beta \sin \beta} - 2t \tan \beta \sin \alpha = 2t \ln \cos \beta = 2t \sqrt{n^2 - \sin^2 \alpha} \quad (3.2)$

Since the phase of the light reflected from the top surface will change by π ,

$$\Delta l_{ef.} = 1 - \lambda/2 \qquad (3.3)$$

when $\Delta l_{ef} = 2K\lambda/2$ or $\Delta l = (2K+1)\lambda/2$, the maximum interference will occur.

By knowing K, λ , α and n, the thickness t can be obtained.

$$t = \frac{K\lambda}{2} / \sqrt{n^2 - \sin^2 \alpha} \qquad (3.4)$$

here K is number of maximum interferences.

For the ZnO thin films, the method described above was used to determine the thickness. During the measurements, the samples were placed under white light or a microscope illuminator and the number of interference rings was counted. Usually, red interference rings were chosen for the calculation because they can be clearly seen under white light. The wavelength of red light is about 7000 Å. Therefore, from eq. 3.4, each red ring represents a thickness increase of about 0.2 microf.

The film thickness also has been measured by using a Dektak surface profiler (Slcan Technology Corp.) to confirm the optical results. During the sputtering, some of the films were prepared

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so that part of the substrate was covered by another piece of glass. When the small needle in the Dektak surface profiler was scanned cross the step, the height of the step was converted into an electrical signal and was recorded by an X-Y recorder.

For the films with a thickness less than 0.2 micron, it is impossible to use the optical method to determine the thickness and the Dektak surface profiler has to be used instead. Generally, for the ZnO films with a thickness greater than 0.5 micron, the optical method can be employed to estimate the thickness of the films.

3.3 X-ray Diffraction

X-ray diffraction technique is an effective method to determine the crystalline structure of a film. It is a nondestructive and noncontact process which gives the information about the presence of phases, film thickness and grain size [3.1][3.2]. The schematic diagram of an X-ray diffractometer is shown in Fig. 3.2.

The X-ray diffractometer consists of a gonoimeter to rotate the sample, an X-ray tube to produce radiation and a counter to detect the radiation spectrum emitted by the sample and to transform into a pulse spectrum. After amplification, the pulse ' spectrum can be converted into a graphic record of intensity

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versus diffraction angle by using an X-Y recorder.

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

(3.5)

$2d_{hkl} \star \sin \Theta = n\lambda$

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Where n is an integer, λ is the wavelength of the incident X-ray, d_{hkl} is the spacing between the crystal planes and θ is the incident angle. The scattered waves interfere with each other and the maximum intensity is achieved when the Bragg condition is satisfied. From the diffraction pattern, the incident angles θ at peak positions can be obtained and the corresponding d values can be calculated from the equation. From the ASTM data, the crystal structure of the film can then be determined.

An X-ray diffractometer (Simens) was used. Experimentally, the glass slide with ZnO film on it was first cut into pieces with a size of 2x2.5 cm². The sample was then mounted onto a glass sample holder using vacuum grease. The sample holder with the the sample was then attacked to the gonoimeter. The diffraction data were collected in a 20 range between 5° and 90° .

3.4 Optical Transmission Measurements

In order to determine the transmission value of the ZnO

thin films, an optical measurement system (see Fig. 3.3) was used. It consists of a Bechman monochromator (model 2400) with a wavelength range from 0.4 to 2.0 microns, an Oriel tungsten lamp source (model 6325). The wavelength of the output was selected by adjusting the position of a prism in the monochromator.

During the measurements, the slit width of the monochromator was maintained at 1.5 mm. A United Detector Si detector (modèl 6-PIN) was used for the intensity measurements. The short circuit current of the detector under illumination was measured using a Keithley (model 480) picoammeter.

The measurement was carried out as follows, the monochromator output was first set at a certain wavelength and the light through a bare glass slide was measured using the Si detector. The same measurement was then done by replacing the bare glass slide with a ZnO-coated glass slide. The transmission coefficient of the ZnO film at this wavelength was obtained by taking the ratio of these two intensity value. The experiments were carried out in a wavelength range from 0.38 to 0.8 micron. It is important to mention that, the reflection factor was not considered for the experiments in this project.

3.5 Electrical Resistivity Measurements

For room temperature resistivity measurements, a four-point

probe technique is conveniently used [3.3]. A schematic diagram of the four point probe use in our laboratory is shown in Fig. 3.4. The four probes are equally spaced and adjusted to the same level. A small current supplied by a dc power supply is passed through the two outer probes and the voltage developed between the two inner probes is measured. The resistivity can be obtained by substituting the thickness W into the following equation,

(3.6)

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 $\rho = V / IWCF$ ohm-cm

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here CF is the correction factor. (when d>>s, CF=4.54.)

The ZnO films were first placed on the plate of the fourpoint probe unit, the probes then were pressed onto the films. Two HP multimeters (model 3468A and 3478A) were used to measure. the voltage across the two inner probes and the current through the two outer probes of the four-point probe unit.

3.6 Hall Effect Measurements

Hall effect measurements can provide informations on carrier concentration and mobility which are important parameters of a semiconductor [3.4]. When the sample with an electrical current I_x flowing in x direction, is placed in a magnetic field, H_z which is perpendicular to the current direction, a Lorentz

force will subject to the carriers in the direction normal to the current and magnetic field plane. If we assume the semiconductor is n type, the field created by the Lorentz force can be

(3.7)

(3.9)

The Hall coefficient and the carrier concentration are related to each other and are given by the following expressions.

 $R_{H}=E_{y}/I_{x}/H_{z} \qquad n=1/qR_{H} \qquad (3.8)$

By knowing the electrical field, the current density and the magnetic field, the Hall coefficient and the carrier concentration can be obtained.

The carrier mobility of the samples also can be obtained from the Hall effect measurements,

 $\mu = \frac{R_{\rm H}}{\rho}$

expressed as

 $E_{y}=I_{x}H_{z}/ne$

Here is the resistivity of the sample.

For thin film measurements, the most effective method was the one developed by Van Der Pauw [3.5][3.6]. The Van Der Pauw method can be described as following. Four point contacts (m, n, p and o) are made on the edge of the hole-free films (see Fig. 3.5). If a current is applied through contacts m and n and the voltage between contacts p and o is measured, the resistance associated with V_{po} and I_{mn} is given by

 $R_{mn,op} = (x_p - V_o) / I_{mn}$

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(3.10)

Similarly, if a current is applied through the contacts n and o, and the voltage between contacts p and \underline{m} is measured, then the resistance associated with these two quantities is given by

$$R_{no,pm} = (V_m - V_p) / I_{no}$$
 (3.11)

Resistivity of the film can then be obtained by using the following equation.

$$= \frac{\pi d}{\ln 2} \frac{(R_{mn,op} + R_{no,pm})_F}{2}$$
(3.12)

where d is the thickness of the film, the factor F is a function of $R_{mn,op}/R_{no,pm}$ [3.5] (see Fig. 3.6).

For Hall coefficient measurements, a current is applied through the contacts m and o, and a potential across the contacts p and n is measured. The resistance $R_{mo,np}$ can be obtained

 $R_{mo,np} = (V_n - V_p)^i / I_{mo}$

(3.13)

the same measurement is repeated under a uniform magnetic field which is applied normal to the surface of the sample. The resistance R'mo, np in the magnetic field is obtained.

It can be shown that the Hall coefficient is proportional to the difference of the resistance.

$$R_{\rm H} = \frac{d}{B} (R_{\rm mo}, np^{-R_{\rm mo}}, np) + /$$
 (3.14)

In our laboratory, a magnet with a magnetic field of about 8 KGauss was used. The sample current and voltage were measured by using the two HP multimeters described before. A low noise switch box was also used to change the contacts to obtain all of the currents and voltages.

For the Hall effect measurements, the glass slides with the ZnO films were first cut into small pieces with a typical size of 2x2.5 cm². Through an Al foil mask, four triangular Al areas were evaporated on the films to form ohmic contacts (as shown in Fig. 3.7). After the Al evaporation, a layer of Wood's metal was evaporated through the same mask by using an Mo boat. The samples were then ready for soldering and measurements.

A ZnO film was then selected and mounted on a sample holder and the four contacts were carefully soldered with four fine Cu wires attached to the sample holder. The measurements were

carried out as following. First, the resistivity of the sample was measured by passing a current through two adjacent contacts (e.g. a and b) and measuring the potential across another two contacts (c and d). Four measurements were made and the was calculated using equation resistivity value for each set 3.10. The final value for resistivity was obtained by taking the average of the four values. After that, the sample was put into the magnetic field. A current was passed through the two contacts located at the two opposite corners (e.g. a and c), the potential difference was measured from another two contacts (b and d). The sample was then moved out from the magnetic field and the same } measurement was repeated under zero field condition. From the difference of the two resistance values (one with magnetic field and the other without), the Hall coefficient was obtained. For the Hall coefficient determination, again, two sets of measurement were made for each sample and the average value was taken.

In order to obtained reliable results, several requirements for the Hall effect measurements using the Van der Pouw method must be satisfied. (1) The contacts must be very small; (2) the contacts are located at the periphery of the films and (3) the film thickness is uniform and free of hole [3.5]. In our experiments, the active area of the films @as isolated from other ynwanted region by scratching the films. This was done also to make sure that the contacts were sufficiently small and located

at the edge of the active area (see Fig. 3.7). Since the

For most of the ZnO samples, the measurements were carried out by using of the two HP multimeters and the readings were recorded manually. In the final stage of the experiments, a Umac 5000 analogue computer connected to an IBM PC was used to measure the current and the voltage values. The constant current required for the measurements was also sent by the Umac. All the calculations were done by the Umac computer and the results were printed by using a EPSON 800 printer.

Using the measurement method described above, the properties of the ZnO films were studied and the results will be presented in next chapters.





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CHAPTER 4 PROPERTIES OF AS-DEPOSITED ZnO FILMS

4.1 Introduction

For photovoltaic applications, it is necessary to have a window material with low resistivity and high optical transmission values. The electrical and optical properties of the ZnO thin films containing In and Al, prepared using the technique described in chapter 2, will be presented in this chapter. Results on the film thicknesses and the crystalline quality will first be described. Following that, results of optical and electrical measurements on the ZnO thin films with different doping concentrations will be presented. For the horizontal samples, a positional effect on resistivity will be specially described. Finally, results of Hall effect measurements of the doped ZnO films will be discussed.

4_2 Thickness Measurements

The thickness of the ZnO thin films was measured by the optical method described in section 3.2. The results for four Indoped samples are shown in Fig. 4.1, where it is clearly seen that the films are not uniform along the substrates. In the

central region, the thickness is much greater than that in the outside area. This effect is specially pronounced for the two samples deposited on horizontal substrates. For the samples deposited on vertical substrates (deposition time 6 hr.), the thickness and its variation are seen to be small. The same thickness measurements were also carried out on Al-doped ZnO thin films and the results are shown in Fig. 4.2. Again, it is seen that the thickness values for the two horizontal samples are larger than that for the vertical ones. Furthermore, the thickness variation for the horizontal samples is larger than that for the vertical ones. In order to confirm the thickness results described above, measurements were also carried out by using a Dektak surface profiler. It was found that the values obtained from the optical measurements are consistent with that using the Dektak surface profiler. Ð

It is thus confirmed that, for the rf sputtered ZnO thin films on horizontal substrates, the thickness of the central region is much larger than the outer region. This thickness variation is due to the small size of the target used in our laboratory (diameter of the target is 4.7 cm).

4.3 Crystal Structure of ZnO films

In order to determine the crystalline quality of the

deposited ZnO films, several samples were examined by X-ray of diffraction. The results for three ZnO samples doped with 2 wt% In are shown in Fig. 4.3. Curves (a) and (b) were obtained for two samples cut from different parts of a horizontal substrate. Curve°(c) was obtained for a vertical one with a thickness comparable to that for sample (b). There are two diffraction peaks for each sample. The relative intensity of the one at 20 of about 35° is much greater than that of the one at about 70°. This intensity effect has been found for all of the samples investigated. By comparing with ASTM data, the ZnO films deposited using the rf magnetron sputtering method in our laboratory were confirmed to be polycrystalline with a wurtzite structure. Furthermore, the films was found to have a (002) preferred orientation. These results are consistent with that reported by other researchers [4.1].

In Fig. 4.3, an intensity difference is also seen for the two samples obtained from two different regions of the horizontal substrate. The height of the diffraction peaks for the samples selected from⁴ the central region is greater than the outer samples. This difference is believed to be due mainly to the difference in thicknesses. For all of the vertical samples examined, the positions of the peaks were observed to be the same as the ones for the horizontal samples. These X-ray results thus suggested that the preferred growth orientation of the ZnO films on substrates without an intentional heating is essentially

independent of the substrate orientation. It is worthwhile to emphasize that the thickness of the vertical sample (c) is approximately the same as that for the horizontal sample (b). The height of the diffraction peaks for (c) is greater than that for (b). Therefore, the crystalline quality of the vertical samples is superior to the horizontal one.

In order to determine the effect of indium in ZnO films, several horizontal samples with different In concentrations were also examined by the X-ray diffraction. For each selected sample, the lattice constant obtained from the main diffraction peak was used to deduce the incremental lattice constant which is plotted as a function of In concentration in Fig. 4.4. One can clearly see that the incremental lattice constant increases with the increase of In concentration. This effect is believed to be due to the large atomic weight of indium atoms added.

4.4 Optical transmission

Fig. 4.5 shows the optical transmission coefficient versus wavelength for a 2n0 thin film doped with 2 wt% In and with a thickness of ^Pabout 1 micron. It is seen that the transmission values increase as the wavelength is increased from 0.4 micron and reach 90% at about 0.5 micron wavelength. When the wavelength is increased further from 0.5 to $0.8^{\frac{1}{2}}$ micron, the transmission

values remain essentially constant. For the ZnO films with higher In concentrations, the optical transmission values are different. Fig. 4.6 shows the results for a sample with 2 wt% In and a sample with 5.3 wt% In. One can see that the cutoff wavelength for the sample with 5.3 wt% In is greater than that for the one with 2 wt% In. Furthermore, the transmission values in the range from 0.5 to 0.8 micron are only about 80% for the sample with 5.3 wt% In. This transmission difference could be due to an increased free carrier absorption in the heavily doped ZnO film [4.2]. The optical transmission characteristics of Al-doped ZnO thin films were also measured and the results were found to be similar to the In-doped ones.

4.5 Resistivity

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As it was mentioned in chapter 1, for photovoltaic applications, low resistivity window materials are required. For the ZnO films, the required low resistivity can be achieved either by controlling the stoichiometry or by introducing impurities. In this section, effects of doping on the electrical resistivity will first be described. A positional effect of resistivity found in the present work will then be introduced.

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4.5.1 Doping Effect

In order to study the doping effect in ZnO, films with different In concentrations were examined by the four point probe method described in section 3.4. The films used were deposited under the fixed conditions and the central areas of the samples were selected for the measurements. In Fig. 4.7, the resistivity of the In-doped ZnO thin films (deposited on horizontal substrates) is plotted versus the In concentration in the target. Here we can see that the resistivity values of the undoped ZnO films are relatively high. As the In concentration is increased to 0.5 wt%, the resistivity decreases to a value of about 0.5 ohm-cm. When the In concentration is increased further to 5.3 wt%, the resistivity decreases by about 2 orders of magnitude. The overall resistivity decrease thus amounts to about 3 orders of magnitude. Therefore, it is very clear that In is an effective dopant for the ZnO thin films. For the deposited horizontal ZnO films with In, the lowest room temperature resistivity observed 2.65×10^{-3} ohm-cm. A similar doping effect was also observed was for the ZnO films containing Al. For the Al-doped films, the resistivity was found to reduce by about 3 orders of magnitude when 2 wt% Al was introduced into the ZnO target.

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4.5.2 Position Effect

, As described in section 4.2, thickness of the 2n0 films was dependent on the position of the substrates. Therefore, it was important and 'interesting to investigate the variation of resistivity with position, especially for horizontal samples. For the horizontal samples, the resistivity was found to vary greatly with the substrate position. This effect is shown in Fig. 4.8, where the resistivity of three samples doped with 2 wt% In is plotted, versus distance from the substrate center. The resistivity values of these three samples are relatively high in the central region and are low in the outer region. The resistivity ratio of the two regions is as high as 2-3 orders of magnitude. Therefore, for low resistivity ZnO film deposition, the substrate must be located in the region about 2 cm from the target center.

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This positional effect on resistivity can be understood as follows. In the central region, the impinging particles have a large vertical momentum component to the substrate. In the outer region, the substrate is not inside the main area of direct projection of the target. Therefore, the vertical momentum component is smaller than that in the central region so that the microscopic quality varies with the distance. The variation of the quality results in the variation of resist wity with the distance. These results are similar to the results reported by to other researchers [1.17].

For the vertical ZnO films with 2 wt% In, resistivity was

also measured versus the distance from the center and the results for three samples are shown in Fig. 4.9. In this figure, it is that the values for two of the samples are essentially seen constant in the entire region. For the other sample, the resistivity increases by a factor of 5 with the distance. The lowest resistivity value is seen to be about 2×10^{-3} ohm-cm..It is interesting to note that, although the vertical films are thinner than the horizontal ones, the resistivity values of the vertical films are generally lower. The lowest resistivity value was obtained on a vertical sample with 2 wt% In (room temperature value was 3x10⁻⁴ ohm-cm). Resistivity measurements of Al-doped ZnO films were also made by the four point probe method. Very similar results were found for the horizontal samples (shown in Fig. 4.10). In Fig. 4.10, the resistivity values in the central region of the substrates are seen to be lower than the outer region and the resistivity difference is about 2 orders of magnitude.

4.6 Hall, Effect

Although the four-point probe method is simple in yielding resistivity results, however, carrier concentration and mobility values can not be deduced. In order to obtained concentration and mobility information, the ZnO films have been examined by using

the Van der Pauw method[®] described before and the results are presented in this section.

4.6.1 Doping Effect

For the Van der' Pauw measurements, samples with different In contents were selected from substrates located at about 3 cm from the target center during the deposition. Resistivity results obtained on these samples are shown in Fig. 4.11. In this figure, we can see that the resistivity is essentially "constant when the In concentration is increased from 0 to 0.5 wt%. And the resistivity decreases when the In concentration is further increased from 0.5 to 5.3 wt%. From the results, it is clear that the resistivity of the films is dominated by the positional effect when In concentration is small. Effect of doping becomes more important only when In concentration exceeds 0.5 wt%. Carrier concentration values were also obtained on these samples and the results are given in Fig. 4.12. Here, the' variation of carrier concentration with the In concentration in the target is obvious. The carrier concentration increases by one order of magnitude as the In concentration is increased from 0 to 2 wt%. However, when the In concentration is further increased from 2 to 5.3 wt%, the carrier concentration remains roughly constant.

The carrier mobility of these ZnO films versus In content is shown in Fig. 4.13. The mobility values are relatively high

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for both the undoped films and those with 0.5 wt% In. The value decreases and remains roughly constant for the films with a In concentration from 2 to 5.3 wt%.

For Al-doped ZnO films, results of resistivity were also obtained by the Van der Pauw measurements. The results showed that the mobility values of the Al-doped films were closed to that of the In doped ones. From the present Hall effect results, the following conclusions are therefore obtained. (1) For the doping levels used in the present work (0 to 5.3 wt%), the , resistivity of ZnO thin films is decreased by the addition of ${}^{igstyle h}$ In and A1. (2) The carrier concentration of the films increases when the In concentration is increased. (3) The mobility decreases by a factor of 5 as the In concentration is increased from 0 to 2 wt%. The concentration increase with doping is believed to be due to the substitution of Zn atoms by group 3 elements (In or Al) which create donor levels. For the undoped films, the excess Zn atoms contribute to free electrons, while for the doped samples, the increased carrier concentration appears to be due to the combination of these two effects. Although the carrier concentration increases as the doping concentration is increased, however, the mobility of the ZnO films is reduced by the presence of impurities.

4.6.2. Position Effect

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The In- and Al-doped (2 wt%) ZnO thin films deposited on the horizontal substrates were also studied by the Van der Pauw method. Several films were selected and six samples were cut from each film for the measurements.

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The results obtained for two different substrates are shown in Fig. 4.14. Here, it is seen that the results are roughly consistent with the results obtained from the four-point probe measurements described in section 4.5. In the central region, the resistivity values are relatively high and the values are low in the region away from the center. In Fig. 4.14, an increase of resistivity is also seen in the region beyond x=3 cm, possibly due to a small sample thickness in this area (less than 0.2 micron).

The mobility of the ZnO films was also found to vary with the distance from the center (shown in Fig. 4.15). In the central region, low mobility values are resulted due to the high vertical impinging momentum of ZnO molecules or atoms. In the region of 2 to 4 cm from the center, the mobility is relatively high. In the region beyond x=4 cm, the thickness is small and the mobility is also small [3.1].

The carrier concentration of the ZnO films was found to remain roughly constant with the distance (see Fig. 4.16). It is also noted that the concentration is greater than 10^{20} cm⁻³ throughout the films.

From the results described above, it is clear that the variation of resistivity with distance in the doped ZnO films is mainly due to the mobility variation. For these films, the carrier concentration remained roughly constant through out the whole substrate. This mobility variation was believed to be due to the difference of the vertical momentum for the impinging molecules or atoms. In the central region, the impinging molecules or atoms have a high perpendicular momentum and resulted in a large defect density in the films. Therefore, the mobility was relatively low. In the outer region, the impinging molecules or atoms hit the substrate with a relatively small perpendicular momentum and formed films with better crystalline quality.

4.7 Conclusions

By using the rf magnetron sputtering technique, good quality ZnO thin films have been obtained on both vertical and horizontal glass substrates. For the films deposited on the horizontal glass substrates, the thickness varied with distance from the substrate center. In the central region, the typical thickness was about 1.5 microns. The thickness was about 1 micron in the low resistivity region. The largest thickness was about 4 microns for a film deposited for a period of 7 hr. For the

vertical samples, the thickness was relatively smaller than the horizontal ones. Furthermore, the thickness values obtained from the optical measurements were found to be consistent with those obtained by using the Dektak surface profiler.

The X-ray results, indicated that ZnO films deposited both on the vertical and horizontal substrates were polycrystalline with a wurzite structure. The two characteristic peaks observed in the range $20 < 80^{\circ}$ indicated that the ZnO films have a (002) preferred orientation. The optical transmission values of ZnO thin films were up to about 90% in the visible wavelength range with a cont-off value at about 0.39 micron. This cut off wavelength value was roughly consistent with the energy gap value of polycrystalline ZnO. Furthermore, the impurity concentration was observed to affect the optical transmission values. The higher the impurity concentrations, the smaller the transmission values.

The present results also confirmed that In and Al are effective dopants (both are group 3 elements) for low resistivity ZnO thin films. The resistivity of the ZnO films was greatly reduced by introducing In or Al cinto the films. For the films with 5.3 wt% In, the resistivity in the central region was found to be about 3 orders of magnitude lower than the undoped ones.

An interesting positional effect on resistivity was also found for the doped horizontal samples. It was observed that the resistivity of the films decreased monotonically with the

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distance from the substrate center. The resistivity ratio of the central and outer regions was found to be as high as 3 orders of magnitude. In the outer region, the lowest resistivity value was about 1×10^{-3} to 3×10^{-3} ohm-cm for the films doped with 2 wt% In. It was also found that the resistivity can be further decreased by depositing on vertical substrates. For such films, a value of 3×10^{-7} ohm-cm has been achieved with 2 wt% In.

The electrical measurements carried out using the Van der Pauw method showed that the main reason for the resistivity variation along the ZnO films was the mobility change in the samples. The carrier concentration was observed to be almost constant along the substrate. Results on the films with different doping concentrations also showed that the carrier concentration increased monotonically with the doping concentration. However, high mobility values were obtained only on samples with a lower doping concentrations.

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Fig. 4.2 Thickness of Al-doped ZnO films plotted as a function of distance from the substrate center.

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Fig. 4.3 X-ray diffraction results of three ZnO films doped with 2 wt% In. /



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Fig. 4.4 Incremental lattice constant plotted versus In concentration in the target for horizontal samples.

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Optical transmission coefficient versus wavelength for a ZnO film with 2 wt% In. Fig. 4.5

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Fig. 4.6 Optical transmission coefficient versus wavelength for two ZnO films with different In doping concentration.



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Fig. 4.7 Resistivity versus In concentration in the target for the horizontal samples, showing the doping effect.



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Fig. 4.10 Resistivity versus distance from the center of the substrate for horizontal ZnO film doped with 2 wt% Al.

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Fig. 4.11 Resistivity versus the in concentration in the target, for the films on substrates located at 3 cm away from the target center, (carrier concentration & mobility shown in Figs. 4.12 and 4.13).



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Fig. 4.15 Carrier mobility versus the distance from the center of the substrates for films with 2 wt% In.

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CHAPTER 5 EFFEGTS OF HEAT TREATMENT ON ZnO FILMS

5.1 Introduction

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Thermal stability is a very important parameter for semiconductor window materials. This is especially true for the films used in solar cells which normally are operated in atmosphere under severe conditions for a long period of time. Good thermal stability is also important for the films during device fabrication which is usually carried out at elevated temperatures.

For undoped low resistivity ZnO thin films, the electrical resistivity was reported by Minami and coworkers [1.18] [5.1] to be relatively unstable at high temperatures. The resistivity of the undoped films increased by about 4 orders of magnitude after a heat treatment at 400°C in vacuum. The increase was even greater when treated in air. Furthermore, they reported that the resistivity of a ZnO thin film containing 2 wt% Al remained essentially constant under the same heat treatment conditions in vacuum. It is therefore specially interesting to know whether the doped low resistivity ZnO films prepared in the present work are also stable at elevated temperatures in air.

For solar cell fabrication involving $I-III-VI_2$ compounds like CuInSe₂, a heat treatment in air at about 200^OC for several hours is usually needed to improve the junction performance. This
heat treatment will not only affect the characteristics of the junction but also the electrical properties of window material. In order to determine the stability of the low resistivity 2n0 films prepared in the present work for the solar cell application with CuInSe₂, heat treatment experiments have been carried out. The results obtained are reported in this chapter.

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5.2 Doping Effect and Air Heat Treatment

In order to study the effect of In doping on the thermal stability of ZnO, several films with different In concentrations were selected and heat treated in atmosphere. During the experiments, a Blue M^* oven with a thermometer was used. The temperature range for the Blue M oven is from 25 to 250°C.

Several samples were first selected and placed in a glass dish with a glass cover. The oven was pre-heated to 250°C and the container with the samples in it was then placed into the oven. After a period of time (for example, 10 minutes), the glass dish with the samples was removed and wrapped by a cotton cloth to cool slowly (at least 20 min.). The room temperature resistivity of the samples was then measured by the four-point probe method

* Product of Blue M Electrical Company.

described before. After the measurements, the heat treatment and electrical measurements were repeated.

The results for several ZnO films with different In concentrations treated at 250°C using the procedure described above are shown in Fig. 5.1. The change of resistivity with the heat treatment time is seen to be dependent on the In concentrations. For the undoped ZnO film, the resistivity increases by two orders of magnitude after the first heat treatment (10 min.) and the value continues to increase with the heat treatment time. However, the resistivity of the ZnO film containing 0.5 wt% In is seen to increases only by 1 order of magnitude. The increase of resistivity decreases with the In concentration. For the film containing 5.3 wt% In, the resistivity remains roughly constant during the complete heat treatment procedure.

For the undoped ZnO films, the donor levels are created by oxygen vacancies [1.12]. During the air heat treatment, oxygen atoms can easily diffuse into the films and compensate these donor levels. For the doped films, however, most of donor levels are created by impurity atoms and it is believed that these are not easily compensated by oxygen atoms at 250°C. Therefore, the resistivity remained constant for the heavily doped ZnO films. From the present results, it is quite evident that the doped ZnO films are much more stable than the undoped ones when treated at 250°C in air.

5.3 Orientation Effect

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As mentioned before, the resistivity of the vertical ZnO samples was lower than that for the horizontal ones. Such low resistivity ZnO films are attractive for photovoltaic cell fabrication. Therefore it is interesting to know their thermal stability in air. The heat treatment experiments have been carried out and the results are described below.

Horizontal and vertical ZnO films with 2 wt% In were first selected and treated in air at 250°C using the procedure described before. The results obtained for two horizontal and two vertical samples are shown in Fig. 5.2. Here the sheet resistance is plotted versus the heat treatment time. For the two vertical samples, the sheet resistance is seen to increase by about 2 orders of magnitude after the first 10 min. heat treatment. However, the sheet resistance of the two horizontal samples remained roughly constant during the heat treatment process.

Although the difference of resistance change between the horizontal and the vertical samples was quite significant, however, it was suspected that this was due to a large difference in thickness. Furthermore, the thermal stability difference also could be due to a substrate orientation effect. In order to determine the dominant factor for the difference, one vertical sample with a thickness comparable to the horizontal •one was

selected and heat treated. The results are shown in Fig. 5.3. We can see that the resistivity of the vertical sample again increases by 2 orders of magnitude after the first 10 min. heat treatment and remains approximately constant during the subsequent process. For the horizontal sample, the resistivity remains essentially constant during the complete treatment procedure. Therefore, the above results suggested that the difference in the resistivity variation between the vertical and horizontal samples is mainly due to an orientation effect.

The observed substrate orientation effect could be due to the following reasons. The density of donor levels from oxygen vacancies for the vertical samples could be greater than that for the horizontal samples. During the heat treatment, the oxygen vacancy levels were compensated by the diffused oxygen atoms. This effect resulted in a drastic decrease in the free carrier concentration and therefore the large increase of resistivity for the vertical samples. From the results described above, it is thus clear that the horizontal ZnO films are more stable than the vertical ones during the treatment in air.

5.4 Temperature Effect

In order to obtain further information on the stability of the doped ZnO films, several horizontal samples have been treated

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in air at different temperatures. The temperature-dependent experiments were made in a range from 200 to 350°C in a step of 50°C. For the treatment experiments at temperatures below 250°C, • the Blue M oven was used. For the treatment experiments at temperatures above 250°C, a Lindberg Heri-Duty tube furnace with a temperature controller was used. For the high temperature heat treatment experiments, the selected samples were placed in a Pyrex tube. The tube with the selected samples were inserted into the furnace and kept in the furnace for a fixed period of time. After the treatment, the tube was removed from the furnace and the samples are allowed to cool slowly.

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The results obtained for six samples are shown in Fig. 5.4. The sheet resistance is seen to remain constant at $200^{\circ}C$ (results at $250^{\circ}C$ which were not shown were also found to be essentially constant). For the two samples treated at $300^{\circ}C$, the sheet resistance increases by 1 order of magnitude after the 2 hr. treatment. An even large increase is seen for the two samples treated at $350^{\circ}C$. The large resistance increase at high temperatures again is consistent with the previously described effect of enhanced oxygen diffusion at the elevated temperatures. From the results described above, it is clear that the air heat treatment of devices involving low resistivity ZnO films must be carried out at temperatures below $250^{\circ}C$ in order to avoid the drastic uncrease of resistivity.

However, the observed temperature-dependent resistivity

variation also could be due to a variation of the crystal quality. To check this factor, preliminary X-ray diffraction experiments were carried out on two samples treated in air (for 1 hr.) at 250 and 350° C respectively. The results of the films treated at 350° C are shown in Fig. 5.5. Here, it is clearly seen that the diffraction peaks are not changed after the 1 hr. heat treatment in air. For the films treated at 250° C, the results are similarly to the ones treated at 350° C. The present X-ray results suggested that the resistivity change is not directly relevant to the change in crystal structure.

5.5 Optical Transmission

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After the air heat treatment, it is also very interesting to know whether the optical transmission values are affected. The optical transmission values of several selected ZnO thin films with 2 wt% In were measured before and after the 2 hr. air heat treatment at 200°C and the results for one of the samples are shown in Fig. 5.6. We can see that the optical transmission coefficients of the ZnO film are essentially not affected by the heat treatment. This result further confirmed that the doped ZnO /films are very stable window materials for optoelectronic devices.

5.6 Effect of Different Treatment Gases on ZnO Films

In order to determine the main reason for the increase of resistivity of the ZnO films after the high temperature air heat treatment, several ZnO thin films containing 2 wt% In were heat treated in pure O_2 and pure N_2 . The experiments were carried out as follows. First the samples were cut into pieces with a size of 2.5x2 cm^2 and the room-temperature resistivity measured. The heat treatment experiments were carried out using a set-up shown in Fig. 5.7. It included a resistively heated furnace, a quartz tube with a diameter of 2.5 cm and a temperature controller. For the heat treatment in nitrogen, the samples were first introduced into the low temperature part of the tube located outside the furnace. Nitrogen gas was then passed through the tube at a rate of about 0.4 liter per minute for at least 10 min. to minimize the oxygen content. The part of tube with the samples was moved to the high temperature zone and treated for a period of 10 or 20 min. After the heat treatment, the part of the tube containing the samples was moved to the original position outside the furnace to cool. A cooling period of at least 15 min. was allowed before removing the samples for measurements. For the heat treatment in oxygen, a procedure similar to the one described above was used.

Several experiments were also made in hydrogen. For the

hydrogen heat treatment, nitrogen was first allowed to flow through the quartz tube for at least 10 min. before introducing hydrogen. This was done in order to avoid the formation of a H_2 and O_2 mixture which is very dangerous at high temperatures. After the first 10 min.; H_2 valve was turned on and the rate controlled to about 0.2 l/min. and the N_2 valve was closed. The H_2 flow was continued for another 10 min. before moving the samples into the furnace for the treatment. After the heat treatment, the tube was withdrawn from the central region of the furnace and the H_2 flow was allowed to continue for at least 10 min. Then the H_2 valve was closed and N_2 was allowed for another 10 min. After the complete procedure, the samples were removed from the tube.

Results of the low resistivity ZnO films treated in different gases are shown in Fig. 5.8. We can see that the resistivity remains roughly constant for the two samples treated in nitrogen. For the two samples treated in air, the resistivity increases by 3 orders of magnitude after a period of 2 hr. For the two samples treated in oxygen, the resistivity increases drastically after the first 10 min. of heat treatment. The resistivity continues to increase during the subsequent heat treatment³⁷ process.

Under normal conditions, the oxygen concentration in air is about 21% (by volume). Therefore, at the same heat treatment temperature, more oxygen atoms (or molecules) in oxygen can

diffuse into the ZnO films to result in the large resistivity increase. From the above results, it is clear that the resistivity increase in air at high temperatures is mainly due to the diffusion of oxygen into the films.

In Fig. 5.9, results of In-doped ZnO thin films treated in air and hydrogen are shown. For the ones treated in air, again the resistivity is seen to increase by three orders of magnitude after a period of 2 hr. For the two samples treated in hydrogen, however, the resistivity varies only very slightly. The results obtained further confirmed the oxygen effect. For the films treated in hydrogen, some of the oxygen atoms in the films may react with the hydrogen atoms. Some resistivity of the ZnO films decreased slightly during the initial hydrogen heat treatment experiment.

The high resistivity ZnO films obtained after the air and oxygen heat treatment were also treated in hydrogen. After a period of 40 min., the resistivity of the samples returned to the original value. Resistivity values of some of the samples were found to be even lower than the original ones.

The resistivity decrease during the hydrogen treatment can be understood as follows. During the heat treatment, hydrogen atoms reacted with oxygen atoms in ZnO films and created new oxygen vacancy levels to give rise to an increase of the free carrier concentration. This effect is especially pronounced for the high resistivity ZnO films obtained after the heat treatment

in an environment containing oxygen. In such high resistivity samples, most of the donor levels were compensated by oxygen atoms. During the hydrogen heat treatment, donor levels were created again and the resistivity was greatly reduced.

Similar experiments were carried out at 350° on Al-doped ZnO films and the results are shown in Fig. 5.10. The resistivity of the two ZnO films remains constant for the heat treatment in nitrogen. For the samples treated in air, the resistivity is seen to increase by about 2 orders of magnitude after the 2 hr. heat treatment. For the two samples treated in oxygen, the resistivity increases by about 4 orders of magnitude. The results shown in Fig. 5.10 are seen to be similar to those given in Fig. 5.8 for the In-doped samples.

5.7 Effects of Heat Treatment on Carrier Concentration and Mobility

In order to obtain more information about the variation of resistivity of ZnO films after the heat treatment, electrical measurements were carried out using a Van der Pauw method. Several samples treated in hydrogen and air at 350°C were specifically examined.

For the In-doped $^{\circ}$ ZnO thin films_k, the results of carrier concentration versus the heat treatment time are shown in Fig.

5.11. For the samples treated in air, the carrier concentration of the films is seen to decrease by about 2 orders of magnitude after the 2 hr. heat treatment. For the two samples treated in hydrogen, however, the carrier concentration remains constant. In Fig. 5.12, the mobility of of two ZnO films treated in air is also seen to decrease by 2 orders of magnitude after the 2 hr. heat treatment. For the two samples treated in hydrogen, the mobility of charge carriers does not change during the heat treatment process.

For the Al-doped ZnO films heat treated in air, the results are shown in Fig. 5.13 and Fig. 5.14. Here, the carrier concentration variation is not very significant. However, the mobility decreases by about 2 orders of magnitude.

For the doped films treated in air at 350°C, the increase of resistivity amounts to about 3 orders of magnitude. It is believed that during the high temperature air heat treatment of these films, not only the oxygen vacancy levels are compensated, some impurity levels are also compensated by the excess oxygen atoms.

The difference in the change of carrier concentration between In- and Al-doped ZnO films could be due to the difference of atomic concentration of impurities. Because the Al atomic concentration in the films with 2 wt% Al_2O_3 is about 3 times of In atomic concentration in the films with 2 wt% In_2O_3 .

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5.8 Conclusions

The thermal stability of ZnO thin films-deposited by the rf sputtering method on glass substrates has been studied. For the ZnO thin films with different doping concentrations, the thermal stability in air at elevated temperatures is quite different. The resistivity of the undoped films increased drastically during the initial period of air heat treatment. For the heavily doped ones, the resistivity remained roughly constant during the heat treatment process. For the doped ZnO thin films, there was a large difference between the vertical and horizontal samples. For the vertical ones, the resistivity remained roughly constant during air heat treatment at temperature below 250°C. For the vertical ones, however, the resistivity values increased by about 2 orders of magnitude after the first 10 min. of heat treatment. Therefore, the present results revealed that the low resistivity doped ZnO films deposited on horizontal substrates are much more stable than the vertical ones.

For the doped horizontal samples, the increase of resistivity was also found to depend on the heat treatment temperatures. When the heat treatment was carried out at a temperature above 250°C, the resistivity values increased continuously with the heat treatment time. For example, for the samples treated at 350°C in air, the resistivity values increased

by more then 3 orders of magnitude after a period of 2 hr. Therefore, in order to avoid the rapid increase of resistivity of the ZnO thin films, the heat treatment should not be carried out at temperatures above 250° C.

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From X-ray diffraction experiments, the crystalline quality of the ZnO films deposited in the present work was found to be essentially not affected by the air heat treatment. The optical transmission values were also observed to remain essentially constant after the air heat treatment experiments. The present results thus suggested that the ZnO films are stable window materials for photovoltaic application.

The heat treatment experiments carried out in different gases confirmed that the increase of resistivity of the ZnO films was mainly due to the diffusion of oxygen atoms. The high resistivity values of the ZnO films obtained from the air heat treatment experiments can be brought back to the original vales by a hydrogen heat treatment.

The resistivity increase of the In-doped ZnO thin films during the high temperature air heat treatment was observed to be due to the decrease of mobility and carrier concentration. For the Al-doped ZnO films, slightly different results were observed. The increase of resistivity in these films was mainly due to the decrease of mobility. Finally, the hydrogen heat treatment was found to maintain the mobility of the films.

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Fig. 5.1 Resistivity of ZnÖ films with different In contents versus heat treatment time, showing effect of In content on the thermal stability of ZnO films.

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Time (minutes)

Fig. 5.2 Sheet resistance of vertical and horizontal samples (In-doped) versus the heat treatment time, showing the superior thermal stability of the horizontal samples.





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ig. 5.5 Relative X-ray diffraction intensity versus 20 for a film with 2 wt% In before and after heat treatment.



Fig. 5.6 Optical transmission versus wavelength before and after heat treatment for a sample with 2% In.



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Fig. 5.8 Resistivity of In-doped ZnO films versus time showing the difference of resistivity increase during the treatment in different gases.



Fig. 5.9 Resistivity of In-doped ZnO films versus time, showing the difference between the air and hydrogen treatment.





Heat Treatment Time (min)

Fig. 5.11

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Variation of carrier concentration with heat treatment time for In-doped samples, two treated in air and the other two treated in hydrogen.



Fig. 5.12

Variation of mobility with heat treatment time for the two samples treated in air and the other two treated in hydrogen (carrier concentration results shown in Fig. 5.11).

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Heat Treatment Time (min)

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Fig. 5.13 Carrier concentration versus time for two Al-doped ZnO films.



CHAPTER 6 CONCLUSIONS

Several important conclusions arising from the present research work on ZnO thin films have been obtained and are summarized below.

(1) Good quality ZnO films have been deposited on glass substrates by using the rf magnetron sputtering technique from the pressed ZnO powder targets containing In and Al. The glass substrates were placed either parallel or perpendicular to the target surface. The typical film thickness of the horizontal samples is about 1 micron for a deposition time of 120 min. The thickness values of the vertical samples were smaller than that, of the horizontal ones under the same sputtering conditions.

(2) From the X-ray diffraction results, it was confirmed that all of the ZnO films showed single phase characteristics with a preferred (002) orientation. The relative intensity of the (002) peak Ancreased with the increase of the film thickness. The X-ray diffraction patterns for the vertical samples were similar to that for the horizontal ones. Furthermore, the X-ray results were not affected by the air heat treatment.

(3) The optical transmission values of the low resistivity ZnO films were determined over the visible range from 0.38 micron to 0.8 micron. The cut-off wavelength was about 0.38 micron (corresponding to the energy gap of polycrystalline ZnO, 3.3 eV) and the transmission values in the wavelength range from 0.5

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micron to 0.8 micron were about 90% for ZnO films doped with 2 wt% In. The values were found to be relatively lower (80%) for the films with 5.3 wt% In. From the present heat treatment results, it was also confirmed that the optical transmission values of the ZnO films were not affected by air treatment.

(4) The electrical resistivity of the ZnO films was greatly reduced by the doping. In the central region of the samples, the resistivity was reduced by about three orders of magnitude when In concentration in the target increased from 0 to 5.3 wt%.

(5) The electrical resistivity of ZnO films was also found to be affected by the position of the substrates. Generally, the resistivity of the vertical samples was lower than that of the horizontal ones. For the horizontal samples, the resistivity was also affected by the distance from the center of the substrates. The resistivity values were found to reduce by 2 orders of magnitude as the distance was 2 cm away from the center.

(6) From the Van der Pauw measurements, it was found that the change of mobility was the main reason for the resistivity variation along the substrate for the horizontal samples. For such samples, the carriers concentration remained to be essentially constant.

(7) In the low resistivity region of the horizontal samples, the resistivity of the films also was reduced by the increase of In doping concentration. However, the carrier mobility of the ZnO[°] films was inversely proportional to the

indium concentration. The carrier concentration of the heavily doped ZnO films was found to be much greater than that for the undoped and lightly doped ones.

(8) The doped ZnQ films were observed to be more stable and the stability improved as the doping concentration was increased. The reason of the drastic increase of resistivity for the undoped samples in the initial stage of the heat treatment process was found to be due to the diffusion of oxygen atoms which compensated the donor levels created by oxygen vacancies. For the heavily doped samples, most of the donor levels were created by the impurity atoms which can not be compensated easily at low temperatures.

(9) The horizontal samples were more stable than the vertical ones at temperatures below 250° C in air. For the horizontal samples, the resistivity remained roughly constant. For the vertical samples, the resistivity increased by more than two orders of magnitude after the air heat treatment at 250 °C. However, the resistivity of the horizontal samples increased more than three orders of magnitude after a treatment for a period of 2 hr. at 350°C. Therefore, in order to minimize the resistivity increase, the treatment temperature must not exceed 250° C.

(10) For the ZnO films with 2 wt% In, the main reason for the resistivity variation during the high temperature $(350^{\circ}C \text{ for example})$ air heat treatment was the decrease of carrier mobility

and concentration. For ZnO films with 2 wt% Al, the resistivity increase was due mainly to the decrease of carrier mobility.

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(11) Heat treatment in hydrogen was found to reduce the resistivity of ZnO films. It is interesting to note that the resistivity values of high resistivity ZnO films resulted from the high temperature treatment (in air or oxygen) can be greatly reduced by the hydrogen treatment.

The present investigation on the rf sputtered ZnO has shown this material to be a good candidate for optoelectronic applications. The required low resistivity for such application can be easily obtained by introducing impurities like In or Al during the deposition. The doping also has an important advantage in improving the thermal stability of the ZnO films. Therefore, the doped ZnO films can be incorporated in devices involving absorbing materials like CuInSe₂.

For device application with CuInSe₂, it is important to note that there is a large lattice mismatch between the two materials. The lattice mismatch between ZnO and CuInSe₂ can be reduced by introducing a layer of CdS or CdZnS between the ZnO and CuInSe₂ [1.6].

The carrier mobility of the present rf deposited ZnO films is still low. More work therefore should be done in order to prepare films with higher mobility and high optical transmission values.

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