

# **FABRICATION, STRUCTURAL AND ELECTRICAL CHARACTERISTICS OF ZINC OXIDE (ZnO) THIN FILMS BY DIRECT CURRENT SPUTTERING**

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## LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
Al	Aluminium
AlN	Aluminium nitride
Al <sub>2</sub> O <sub>3</sub>	Sapphire
Ar	Argon
AZO	Aluminium zinc oxide
CVD	Chemical vapor deposition
DC	Direct current
EDX	Energy dispersive x-ray analysis
FWHM	Full width at half maximum
Ga	Gallium
GaN	Gallium nitride
HCl	Hydrochloric acid
Hcp	Hexagonal close packed
H <sub>2</sub> O	Water
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
HF	Hydrofluoric acid
In <sub>2</sub> O <sub>3</sub>	Indium oxide
ITO	Indium tin oxide
I-V	Current-voltage
LD	Laser diode
LED	Light emitting diode
Li	Lithium
Na	Sodium
NH <sub>4</sub> OH	Ammonium hydroxide
MBE	Molecular beam epitaxy
MgO	Magnesium oxide
N <sub>2</sub>	Nitrogen
NH <sub>3</sub>	Ammonia
O <sub>2</sub>	Oxygen
P	Phosphorous
P <sub>2</sub> O <sub>5</sub>	Phosphorous pentoxide
PEMOCVD	Plasma enhanced metal organic chemical vapor deposition
PLD	Pulse laser deposition
RF	Radio frequency
RMS	Root mean square
RT	Room temperature
SEM	Scanning electron microscopy
Si	Silicon
SiO <sub>2</sub>	Silicon dioxide
SnO <sub>2</sub>	Stannic oxide
TCO	Transparent conductive oxide
UV	Ultra violet
SPD	Spray pyrolysis deposition
XRD	X-ray diffraction
Zn	Zinc
ZnO	Zinc oxide
ZnS	Zinc sulfide
ZnSe	Zinc selenide
Zn <sub>3</sub> N <sub>2</sub>	Zinc nitride

## LIST OF SYMBOLS

$\beta$	Full Width at Half Maximum FWHM
$\lambda$	Wavelength.
$\theta$	Bragg diffraction angle
$a$	Lattice constant in a plane
$c$	Lattice constant in c plane
$D$	Mean grain size
$at.$	Atomic
$E_g$	Energy gap
$n$	Integer
$V_o$	Oxygen vacancy
$Zn_i$	Zinc interstitial

# **FABRIKASI, CIRI-CIRI STRUKTUR DAN ELEKTRIK FILEM NIPIS ZINK OKSIDA (ZnO) OLEH PERCIKAN ARUS TERUS**

## **ABSTRAK**

Semikonduktor jurang tenaga lebar zink oksida (ZnO) telah muncul sebagai bahan yang berpotensi untuk pelbagai aplikasi termasuklah sebagai peranti opto-elektronik seperti diod pemancar cahaya, diod laser dan pengesan. Terdapat banyak lagi yang perlu diterokai dan difahami tentang ZnO sebelum peranti-peranti ini boleh dikomersilkan. Paling ketara, pendopan jenis p bagi ZnO masih lagi menjadi isu disebabkan oleh ZnO yang sememangnya wujud sebagai jenis n. Namun, apabila pendopan jenis p diperolehi, ZnO dapat digunakan di dalam pelbagai bidang seperti yang dinyatakan di atas. Matlamat projek ini adalah untuk mensintesis pendopan serentak ZnO di dalam bentuk filem nipis dengan menggunakan teknik percikan magnet arus terus dan mengkaji ciri-ciri struktur serta elektrik. Teknik percikan serentak bagi 99.99 % tulen target zink dan 99.99 % tulen aluminium asli dimendapkan ke atas substrat silikon. Kemudian, filem-filem nipis tersebut menjalani proses sepuhlindap pada suhu yang berlainan di antara 200 °C hingga 600 °C dengan nisbah gas nitrogen dan oksigen yang berbeza. Ciri-ciri struktur dan elektrik bagi filem- filem nipis ZnO dicirikan oleh mikroskop daya atom (AFM), mikroskop imbasan elektron (SEM), pembelauan sinar-X (XRD) dan pengukuran kesan Hall. Daripada keputusan yang diperolehi, kesemua filem zink telah menjadi ZnO seperti yang disahkan oleh XRD dan filem konduksi jenis p berjaya dihasilkan dengan kaedah pendopan oleh Al-N. Hasil ini juga menunjukkan bahawa struktur filem adalah sangat dipengaruhi oleh suhu sepuhlindap dan nisbah nitrogen dan oksigen yang digunakan. Keputusan yang diperolehi daripada AFM mendapati bahawa kekasaran struktur permukaan semakin menurun apabila suhu sepuhlindap meningkat dengan kehadiran nitrogen yang banyak. Walau bagaimanapun, SEM menunjukkan perubahan yang ketara pada struktur permukaan filem nipis apabila suhu sepuhlindap meningkat dari 200 °C

hingga 600 °C dengan kehadiran oksigen dan nitrogen. Filem yang disediakan dengan nisbah 50% N<sub>2</sub> : 50% O<sub>2</sub> dan disepuhlandap pada suhu 200 °C selama 1 jam mempunyai kerintangan paling rendah iaitu  $1.530 \times 10^{-3} \Omega \cdot \text{cm}$  dan ketumpatan pembawa paling tinggi iaitu  $+1.85 \times 10^{22} \text{ cm}^{-3}$ .

# FABRICATION, STRUCTURAL AND ELECTRICAL CHARACTERISTICS OF ZINC OXIDE (ZnO) THIN FILMS BY DIRECT CURRENT SPUTTERING

## ABSTRACT

The wide band gap semiconductor of zinc oxide (ZnO) has emerged as a potential material for the fabrication of a range of devices including opto-electronic devices such as light – emitting diodes (LEDs), laser diodes (LDs) and detectors. There is still much to be explored and understood about ZnO before such devices can be commercially realized. Most notably, p-type doping of ZnO remains an issue, as does the origin of the native n-type conductivity. Nevertheless, when p-type doping is obtained in ZnO it could be used in various applications as mentioned above. The goals of this project were to synthesize codoped ZnO in the forms of thin films by using direct current (DC) magnetron sputtering deposition technique and to study the structural and electrical properties. A 99.99 % pure zinc target and 99.99 % pure rods of aluminium were sputtered on silicon substrates using the direct current (DC) co-sputtering technique. The films were then annealed in different ratios of nitrogen and oxygen at annealing temperatures in the range of 200 °C to 600 °C. The structural and electrical properties of ZnO thin films grown were then characterized by atomic force microscopy (AFM), scanning electron microscope (SEM), X-ray diffraction (XRD) and Hall Effect measurements. From the results, all Zn films were fully converted to ZnO as confirmed by XRD and film with p-type conduction was successfully produced by the Al-N codoping method. This work also indicates that the film surface characteristics are strongly influenced by the annealing temperatures and the ratios of nitrogen and oxygen used. From the results obtained by AFM, the roughness of the surface structure decreased with increasing of annealing temperature in the presence of large amount of nitrogen. However, SEM revealed the distinct change on thin film surface when the annealing temperature increased from 200 °C to 600 °C in the presence of oxygen and nitrogen. P-type ZnO thin films prepared at N<sub>2</sub>-to-O<sub>2</sub> ratio of 50% : 50%

and annealed at 200 °C for 1 hour showed the lowest resistivity of  $1.530 \times 10^{-3} \Omega \cdot \text{cm}$  and the highest carrier concentration of  $+1.85 \times 10^{22} \text{ cm}^{-3}$ .

# CHAPTER 1

## INTRODUCTION

### 1.1 II-VI semiconductor compounds

II-VI compound semiconductors had always been an interesting classification of semiconductors. For over a decade, II-VI semiconductors have attracted growing interest owing to their possible application in opto-electronics. The wide band gap II-VI semiconductors are efficient emitters in the blue to ultra-violet (UV) spectral range and are likely candidates to replace materials like GaN in light emitting laser diodes (Gutowski, 2002). Despite some similarities, each of the II-VI semiconductors demonstrates their own unique and novel physical properties. These compounds mostly crystallize in the cubic (zinc blende) or hexagonal (wurtzite) structure. These structures occur in a wide range of various band gaps and lattice constants as shown in Table 1.1.

The band gaps have a major influence on the properties of the material. This includes the properties like optical absorption, electrical conductivity and index of refraction. Materials are normally classified according to the type of band gap as direct or indirect semiconductors. The direct band gap semiconductors are found to be advantageous over indirect band gap semiconductors, as they do not require phonons to satisfy wave vector conservation. Most of the II -VI compounds are found to exist as direct band gap semiconductors and have been dominating the optical field for short wavelength applications. They are used in various applications such as light emitting diode (LEDs) and ultraviolet photodetector (Fasol, 1997), UV blue semiconductor laser (Bagnall, 1997) and so on.

A common characteristic that all II-VI semiconductors share is an ability to form into the wurtzite crystal structure. The structural characteristics of wurtzite can be illustrated

by zinc sulfide (ZnS). The structure of ZnS, for example, can be simply described as a number of alternating planes composed of tetrahedrally coordinated  $S^{2-}$  and  $Zn^{2+}$  ions, stacked alternatively along the c-axis (figure 1.1 (a)). ZnS has band gap energy of 3.6 eV (Pawaskar, 2002), displays a high refractive index and high transmittance in the visible range (Falcony, 1992, Xu, 1999), thus become a strong candidate for use in opto-electronic devices. They are still the only materials with which green lasers could be obtained.

Zinc blend is the second common structure for the II-VI compound semiconductor (figure 1.1 (b)). Bulk ZnS, for example, is the most typical example of the structure.

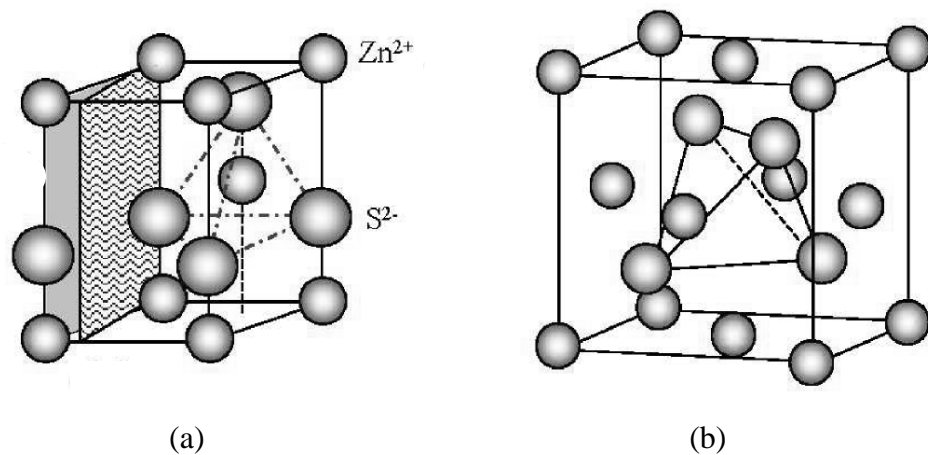


Figure 1.1 (a) The wurtzite ZnS structure and (b) the zinc blend structure for the II-VI semiconductors (Ma, 2004).

Zinc oxide (ZnO) is also one of the II-VI compounds with some exceptional and comparable properties to their III-V counterparts. In Table 1.1, the properties of the most popular wide band gap semiconductors are compared.



Table 1.1 Comparison of the properties of ZnO with that of other wide gap semiconductors (Chen, 1998).

Material	Structure	Lattice constant		Band gap at RT (eV)
		a (Å)	c (Å)	
ZnO	Wurtzite	3.249	5.207	3.37
ZnS	Wurtzite	3.823	6.261	3.80
ZnSe	Zinc blende	5.668	-	2.70
GaN	Wurtzite	3.189	5.185	3.39
6H – SiC	Wurtzite	3.081	15.12	2.86

## 1.2 The research objective

To realize the light emitting devices, an important issue to be resolved is the fabrication of p-type ZnO with a high hole concentration and a low resistivity. However, achieving p-type material is not an easy task due to the self-compensated effect of the native defects. There has been work that focused on the synthesis of p-type ZnO doped with N (Guo, 2001, Ryu, 2000). Minegishi et.al (1997) reported the p-type ZnO films grown by chemical vapor deposition from a powder of ZnO source where the N source was NH<sub>3</sub> with purified hydrogen gas acting as carrier. The resulting p-type ZnO films showed hole concentration of  $1.5 \times 10^{16} \text{ cm}^{-3}$  and a resistivity of 100  $\Omega \cdot \text{cm}$ . Since then, several works were engaged in this investigation of codoping method. More works are still needed in order to produce a viable p-type ZnO and to understand the formation and its behaviour.

In view of the above, present work involves an investigation to produce p-type ZnO by using DC magnetron sputtering via codoping method by utilizing aluminium (Al) as a donor and nitrogen (N) as an acceptor. As most of the research has been focused at annealing temperature of above 700 °C, we will be investigating the role of lower annealing temperature (< 700 °C) with different gas ratios of nitrogen and oxygen on the structural and electrical properties of ZnO thin films. Some of the ZnO films will be grown on p-type (111) silicon substrates since it offers a very attractive opportunity to

incorporate future ZnO-based devices onto silicon-based integrated circuits even though sapphire and glass substrates could produce better quality ZnO films. This work will involve the deposition of Zn from Zn target with Al incorporation by DC magnetron sputtering. The annealing will be performed at varied temperature from 200 °C to 600 °C to realize Al-N codoped ZnO with the flow of nitrogen and oxygen gases at different ratio such as 10:0, 7:3, 5:5 and 0:10. The surface morphologies of the ZnO film are to be investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) while the crystallinity of the films will be determined by X-ray diffraction (XRD) analysis. The energy dispersive X-ray (EDX) will be used for compositional analysis of the fabricated ZnO films. The carrier's concentration and mobility as well as the electrical resistivity of the films will be investigated by using the Hall measurement technique whereby the results obtained would be correlated with the structural properties of the ZnO films.

### **1.3 Outline of the thesis**

Chapter 1 provides the introduction that includes the objective of the present work.

Chapter 2 discusses in detail the properties of zinc oxide, current issues about the development of zinc oxide and its application, literature survey on the various techniques followed by sputtering theory and current state of research in zinc oxide.

Chapter 3 describes the processing technique and the description of the procedures involved in fabricating codoped zinc oxide films.

Chapter 4 presents the results obtained in this work and the related discussion.

Chapter 5 summarizes conclusions drawn from this research and provides suggestions for future work improvements.

## CHAPTER 2

### LITERATURE REVIEW

#### **2.1 The introduction of zinc oxide (ZnO)**

The growth and characterization of II-VI semiconductor ZnO and ZnO-based alloys including MgZnO, CdZnO and MnZnO have been actively investigated for the last three decades or so for its promising semiconductor device applications in the electronics as well as optoelectronics operating in the blue and ultraviolet (UV) region of the light spectrum. The focus on the II-VI semiconductor have been motivated by the lack of semiconductor materials satisfying commercial demands for blue, green and UV lasers and light emitting devices in last decades. The research works have been also encouraged by explosion of demands on various applications such as flat panel displays (Ghis, 1991), solar cell (Sang, 1998), gas sensor (Dayan, 1998) and surface acoustic wave devices (Gorla, 1999).

It is known that producing p-type ZnO is difficult because of its tendency to be n-type. As grown ZnO is n-type due to structural defects from the growth process, such as oxygen vacancies, zinc interstitials, and antisites. An antisite occurs when a nucleus of one species occupies a lattice site that is typically occupied by another species, such as a zinc nucleus on an oxygen site in the lattice. A vacancy is an unoccupied lattice site, resulting in unsatisfied bonds within the lattice. An interstitial defect is a nucleus that does not occupy a lattice site, perturbing the periodic potential that gives rise to the ideal band structure. The ZnO has wurtzite hexagonal structure as shown in figures 2.1 and 2.2, with a wide band gap of 3.37 eV at room temperature. Table 2.1 indicates the properties of the ZnO and other popular wide band gap semiconductors (Chen and Yao, 1998).

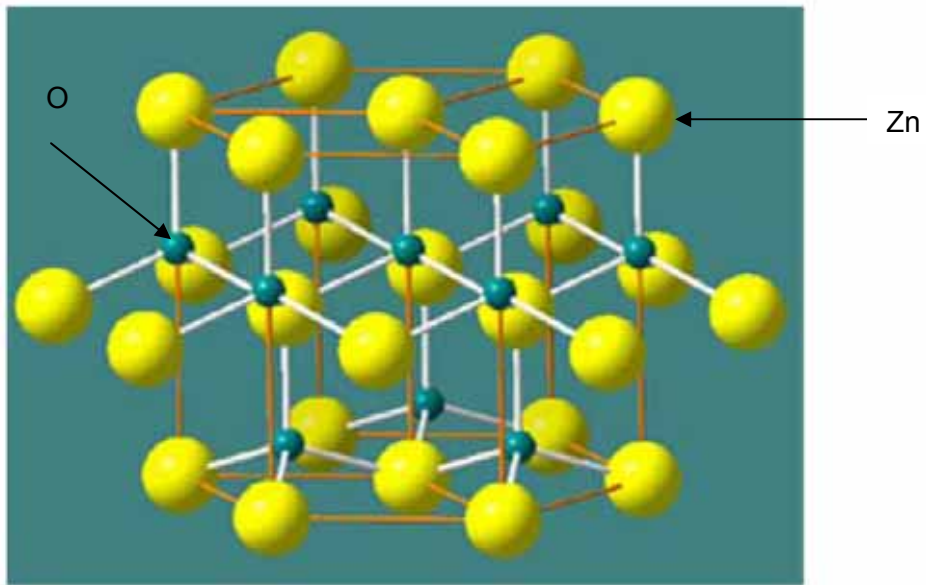


Figure 2.1 Wurtzite structure of ZnO (large ball – Zn, small ball – O) (Kaldis, 1981).

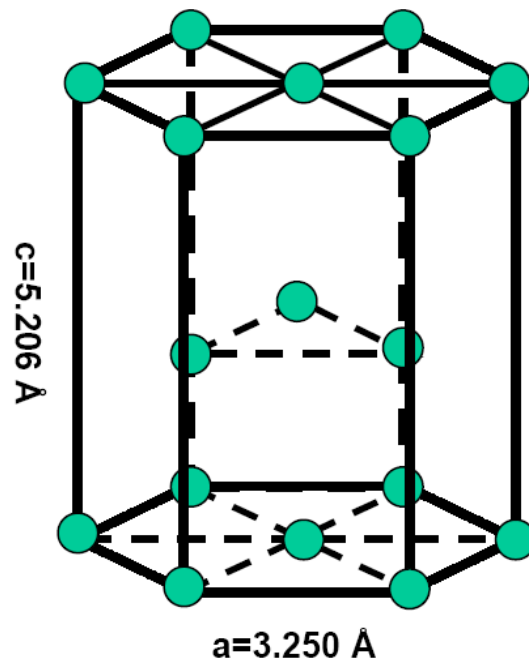


Figure 2.2 Hexagonal close – packed (hcp) structure of ZnO (Kaldis, 1981).

The most desirable feature of zinc oxide is to have the largest exciton binding energy of 60 meV as compared to 24 meV for GaN, which is the key parameter that enables the UV laser diode and other exciton related light emitting devices to be operated at room temperature and makes ZnO a brighter emitter. Unlike GaN, ZnO can be grown in bulk, also compatible with wet etchants and does not need dry etching. ZnO is one of the “hardest” materials in II – VI compound semiconductors due to the higher melting point and large cohesive energy. It can be expected that a degradation of the material due to the generation of dislocations during the device operation will be reduced. The constituent elements of ZnO are abundant and of low cost. Also the material is nontoxic, which is an important consideration for environment.

Table 2.1 Comparison of the properties of ZnO with that of other wide band gap semiconductors (Chen, 1998).

Material	Structure	Lattice constants		Bandgap at RT (eV)	Cohesive energy (eV)	Melting point (K)	Exciton binding energy (meV)	Dielectric constant
		a (Å)	c (Å)					
ZnO	wurtzite	3.249	5.207	3.37	1.89	2248	60	$\epsilon(0)=8.75$ $\epsilon(\infty)=3.75$
ZnS	wurtzite	3.823	6.261	3.8	1.59	2103	39	$\epsilon(0)=9.6$ $\epsilon(\infty)=5.7$
ZnSe	Zinc blende	5.668	—	2.70	1.29	1793	20	$\epsilon(0)=9.1$ $\epsilon(\infty)=6.3$
GaN	wurtzite	3.189	5.185	3.39	2.24	1973	21	$\epsilon(0)=8.9$ $\epsilon(\infty)=5.35$
6H-SiC	wurtzite	3.081	15.117	2.86 (ind)	3.17	>2100	—	$\epsilon(0)=9.66$ $\epsilon(\infty)=6.52$

## 2.2 Some current issues about the development of ZnO research

### 2.2.1 Substrates

One of the major problems which always affect the progress of ZnO research has been lack of a suitable material that is lattice matched to the ZnO. It has been established that the crystal structure of epitaxial ZnO is most strongly influenced by the substrate used.

Currently, the most common substrate material used for the growth of ZnO is sapphire (or  $\text{Al}_2\text{O}_3$ ), despite having a lattice mismatch between the ZnO and sapphire of 18.4% (Ozgur, 2005). The crystal structure of sapphire is shown in figure 2.3. The use of sapphire is most probably due to its low cost, its ease of handling, its transparent nature, hexagonal symmetry with lattice constant of  $a = 4.785 \text{ \AA}$  and  $c = 12.991 \text{ \AA}$  and its stability at high temperatures.

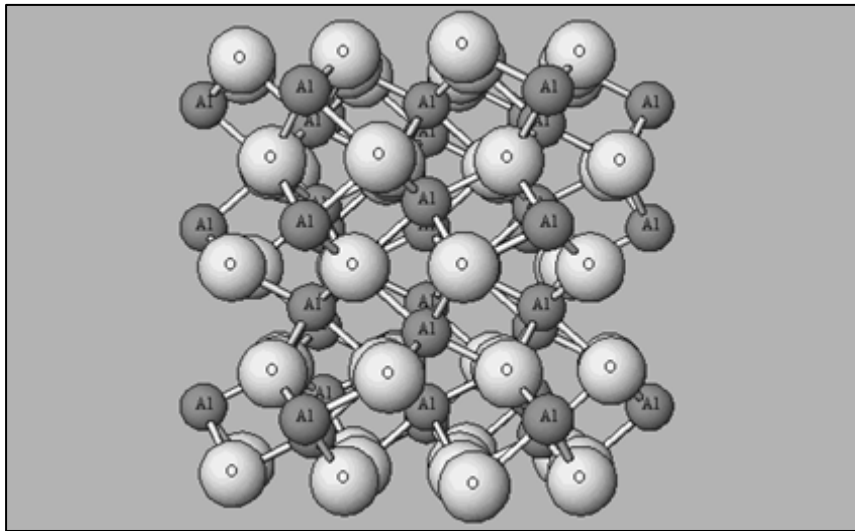


Figure 2.3 The hexagonal crystal structure of sapphire (Imawa, 1982).

Other than sapphire, the other commonly used substrates for ZnO epitaxy is AlN. AlN is a wide band gap III-V semiconductor with direct band gap of 6.2 eV at room temperature (Yamashita, 1979) and has hexagonal structure with lattice constant of  $a = 3.111 \text{ \AA}$  and  $c = 4.982 \text{ \AA}$  as shown in figure 2.4. Due to its large band gap, AlN is transparent from infrared to near UV wavelengths (3 to 0.3  $\mu\text{m}$ ) and can be used as window material for near UV and infrared. AlN has high thermal conductivity, high resistivity and low thermal expansion. It has the potential for the applications in high performance electronic industry as integrated circuit package and heat sinks. However, some disadvantages such as its high cost and the small number of available manufacturers which produce AlN have made AlN less popular as a substrate for ZnO from a manufacturing point of view.

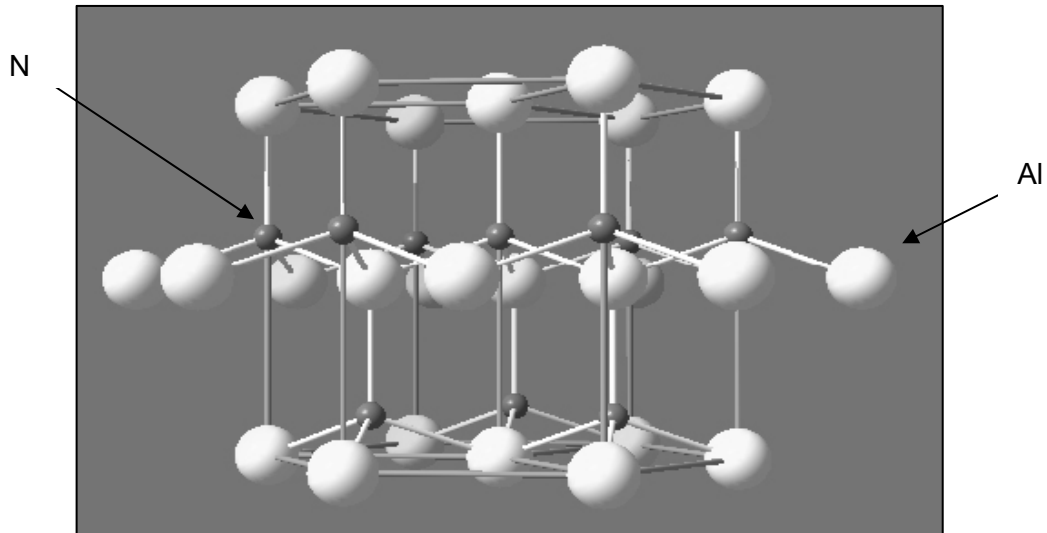


Figure 2.4 Hexagonal wurtzite structure of AlN (Large ball-Al, small ball-N) (Imawa, 1982).

At present, most of the commercial electronic devices are based on silicon. The development of modern semiconductor industry leads to much matured techniques for producing and processing high quality silicon wafers. Besides being used extensively in semiconductor industries, silicon is also widely used in the scientific research, either as subjects aimed for the generation of new silicon based devices or as substrate materials for developing other new functional materials. Figure 2.5 shows a schematic of diamond silicon crystal structure with lattice constant of  $a = 5.430 \text{ \AA}$ . Silicon is widely used as substrates in thin film growth processes because the material is much cheaper as compared to other single crystalline materials (examples sapphire, AlN, MgO etc). Large size silicon wafers can be obtained commercially with low cost and can be cut to any size to fit the requirements of deposition process. It is highly desired to integrate semiconductor thin films with silicon substrates. In this case, most of the advantages of modern semiconductor industries can be used in the later device development. Furthermore modern semiconductor industry can provide low cost silicon wafers with various properties required by customers.

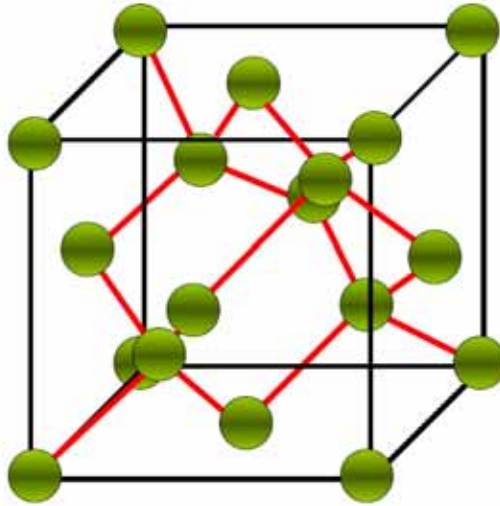


Figure 2.5 Schematic diamond crystal structure of silicon (Iwama, 1982).

### 2.2.2 Doping of ZnO

Doping has always been an issue in wide band gap materials because as the band gap of a material increases it becomes difficult to dope them in symmetry (p-type and n-type). For example, doping diamond p-type is very easy as compared to that of n-type. Similarly, there are quite a few issues in doping p-type GaN while it is easier to make n-type GaN. However, wide band gap of ZnO materials pose special challenges in getting p-type semiconductor.

ZnO with a wurtzite structure is naturally an n-type semiconductor because of a deviation from stoichiometry due to the presence of intrinsic defects such as O vacancies ( $V_o$ ) and interstitials ( $Zn_i$ ). Undoped ZnO shows intrinsic n-type conductivity with high electron densities of about  $10^{21} \text{ cm}^{-3}$  (Minami, 1985). It is externally doped to produce films of higher conductivity and high carrier concentrations. Many researchers have worked on doping ZnO n-type using group III elements like aluminium (Al), gallium (Ga) and indium (In) (Chang, 2003). This process was found to produce ZnO films with more n-type conductivity, improving its transparency and conductivity. A study by Igasaki et.al (2001) proved that doping of ZnO had improved not only the



electrical properties of the film but also its thermal stability. Among all n-type dopants being used, aluminium is found to be the best dopant as it produces films with the highest conductivity and transparency as compared to any other dopant. Aluminium doped zinc oxide (AZO) is deposited using various techniques such as pulsed-laser deposition, radio frequency (rf) magnetron sputtering, chemical vapor deposition, spray pyrolysis and the sol-gel process.

On the other hand, efforts to obtain p-type doping have resulted in heavily compensated and highly resistive films, which cause the development of a reliable p-type doping technique for ZnO remains a primary challenge for researchers. The difficulties can arise from a variety of causes. Dopants may be compensated by low energy native defects, such as  $Zn_i$  or  $V_o$  (Walukiewicz, 1994). Low solubility of the dopant in the host material is also another possibility. Deep impurity level can also be a source of doping problem, causing significant resistance to the formation of shallow acceptors.

Known acceptors in ZnO include group I elements such as lithium (Li) ( Schimer, 1968, Valentini, 1991, Zwingel, 1970), sodium (Na), silver (Ag) and group V elements such as nitrogen (N) and phosphorus (P). However, many of these do not contribute significantly to p-type conduction. It is believed that the most promising dopants for p-type ZnO are the group V elements, although theory suggests some difficulty in achieving shallow acceptor level (Park, 2002).

A number of groups have expended a good deal of effort in an attempt to realize p-type ZnO using nitrogen (N) as a possible shallow acceptor dopant. Various type of nitrogen sources including  $N_2$ , NO,  $N_2O$ ,  $NH_3$  and  $Zn_3N_2$  have been used depending on the growth technique. Iwata et.al (2000) has attempted p-type doping of ZnO using molecular beam epitaxy (MBE) by simultaneously introducing  $O_2$  and  $N_2$  through a rf

plasma source. Although a carrier concentration as high as  $10^{19} \text{ cm}^{-3}$  was obtained, p-type conduction was not achieved. However, some promising results were reported recently. Look et.al (2002) reported p-type ZnO by MBE with N doping using Li-diffused semi-insulating ZnO substrates and an  $\text{N}_2$  rf plasma source.

Li et.al (2003) claimed to have succeeded in p-type doping of ZnO films, by reacting diethyl zinc (DEZn) with NO gas. In this case, NO gas was used to supply both O and N for p-type doping. Results indicated that N can be incorporated into ZnO films without plasma or high temperature process and a high N concentration was obtained only under Zn rich conditions as predicted by Yan et.al (2001). Nevertheless, reproducibility still remains to be a major problem and this must be resolved before ZnO can be used in opto-electronics applications such as homojunction LEDs and laser diodes (LDs).

### **2.3 Applications of ZnO**

Zinc oxide (ZnO) is no stranger to scientific study. In the past 100 years, it has been featured as the subject of thousands of research papers, dating back as early as 1935 (Bunn, 1935). Valued for its ultra violet absorbance, wide chemistry, piezoelectricity and luminescence at high temperatures, ZnO has penetrated far into industry and is one of the critical building blocks in today's modern society (Lide, 1992). It encompassed applications in paints, cosmetics, plastic and rubber manufacturing, electronics and pharmaceuticals.

Research on this material revealed that its properties like crystal structure, band gap and some of its physical and electrical properties are favourable to the extent of replacing some of the materials that are being used as lasers and as window layers in solar cells. A brief comparison of zinc oxide with other materials with similar applications is described in the following sections.

### 2.3.1 Zinc oxide as transparent conductive oxides (TCO)

Zinc oxide, besides being one of the important materials in the classification of wide band gap materials, is one of the important transparent conductive oxides (TCO). Being abundant in nature it is available at lower cost compared to tin and indium, the increasing used materials as TCOs. It has the added advantage of being non-toxic and it can be deposited at relatively low temperatures. Zinc oxide has very good optical and electrical properties. According to Lee et. al (2002), these properties for ZnO could be either a match or exceed the properties for tin or indium tin oxide (ITO). TCO such as indium-tin-oxide (ITO), Al-doped zinc oxide (AZO) and Zn-doped indium oxide (IZO) have attracted much interest in the application of optoelectronic devices such as solar cells and liquid crystal displays due to their high conductivity and high transparency in the visible region.

Table 2.2 Some properties of transparent conducting oxides at room temperature.

Compound	Structure type	Cell dimensions (Å)			Resistivity $\Omega.cm$	Band – gap (eV)	Refractive index
		a	B	c			
SnO <sub>2</sub>	Rutile	4.7371	-	3.1861	$10^{-2} - 10^{-4}$	3.7 – 4.6	1.8 – 2.2
InO <sub>3</sub>	Bixbyite	10.117	-	-	$10^{-2} - 10^{-4}$	3.5 – 3.75	2.0 – 2.1
ITO	Bixbyite	10.117-10.310	-	-	$10^{-3} - 10^{-4}$	3.5 – 4.6	1.5 – 2.1
CdSnO <sub>4</sub>	SrPbO <sub>4</sub>	5.5684	9.8871	3.1933	$10^{-3} - 10^{-4}$	2.7 – 3.0	2.05 – 2.1
ZnO	Wurtzite	3.2426	-	5.1984	$10^{-1} - 10^{-4}$	3.1 – 3.6	1.85 – 1.90

The other major disadvantage of TCO is that it has less light-trapping ability leading to a limitation in cell performance. Muller et al (2000) have found that a post deposition chemical etching step textures of ZnO: Al films resulted in lowering the resistance of these films. It is also found that these films when incorporated in amorphous-Si solar cells produced an initial efficiency that is higher than commercially available TCO substrates. This is the important reason that prevents TCO from being used for large area module manufacturing (Muller, 2001, Ryu, 2000). With these advantages, the

usage of ZnO and Al-doped ZnO is increasing in the industry today. Table 2.2 shows some properties of TCOs (Bube, 1986).

### **2.3.2 Zinc oxide for opto-electronics**

Gallium nitride (GaN) is used as the major source for blue lasers since the mid 1990s. It is also used extensively in fabricating devices like piezoelectric and waveguide devices, light emitting diodes and photodetectors. However, ZnO has emerged as a possible competitor in opto-electronic applications as the structure and the band gap of zinc oxide prove promising for these applications. Studies have proved that ZnO could be used as the substrate for GaN films as both the materials share the same structure (Ryu, 2000). The exciton binding energy, the important property for any optical device like LEDs and lasers is 60 meV in ZnO, which is 2.4 times that of GaN. This is the reason why ZnO is considered as a prospective candidate for these devices (Zhang, 2002). Apart from these optical properties, ZnO has some interesting physical properties that have made it more attractive in this field. With a melting point of 2000 °C, it is sufficiently stable at high temperatures. This is an important requirement during doping and formation of ohmic contacts. The higher hardness, resistance to mechanical stress and high melting point temperature of a material also expand the lifetime of LEDs and blue laser diodes (Ryu, 2000). Therefore, ZnO as a potential wide band gap material can be used in short wavelength light emitting devices such as light emitting diodes, photodetectors, electroluminescence devices and the next generation of UV semiconductor lasers (Zhang, 2002).

Table 2.3 highlights some of the keys properties of ZnO and provides the comparison with GaN. The factor of p-type doping in ZnO has initiated the interest for this research. A brief description of doping and the work by many researchers on this topic is further discussed in this chapter.

Table 2.3 The comparison between ZnO and GaN (Ozgur, 2005).

Property	ZnO	GaN
Energy band gap, $E_g$ (eV)	3.37	3.39
RT exciton binding energy $E_B$ (meV)	60	25
RT stable phase	Wurtzite	Wurtzite
$a_o$ (Å)	3.25	3.12
$c_o$ (Å)	5.21	5.19
Bulk growth	Yes	Difficult
Epitaxial growth	Yes	Yes

## 2.4 Deposition techniques

ZnO films can be deposited by a variety of techniques such as:

2.4.1 *Plasma-Enhanced Metalorganic Chemical Vapor Deposition (PEMOCVD)*: (Dhar, 2005, Vispute, 1998).

PEMOCVD is one of the most attractive techniques for synthesis of high perfection ZnO films at low and moderate temperatures. The system consists of continuously pumped horizontal quartz tube placed between copper plates to which RF power (13.56 MHz) is used to excite plasma in the reaction chamber and to dissociate Zn vapor. The base unit is equipped with a resistive-heated evaporator where quartz ampoule containing Zn is placed. Figure 2.6 shows a schematic of the plasma reactor for this technique. Crystalline sapphire (001), silicon (100) and  $\text{SiO}_2/\text{Si}$  substrates can be used for deposition of ZnO thin films.

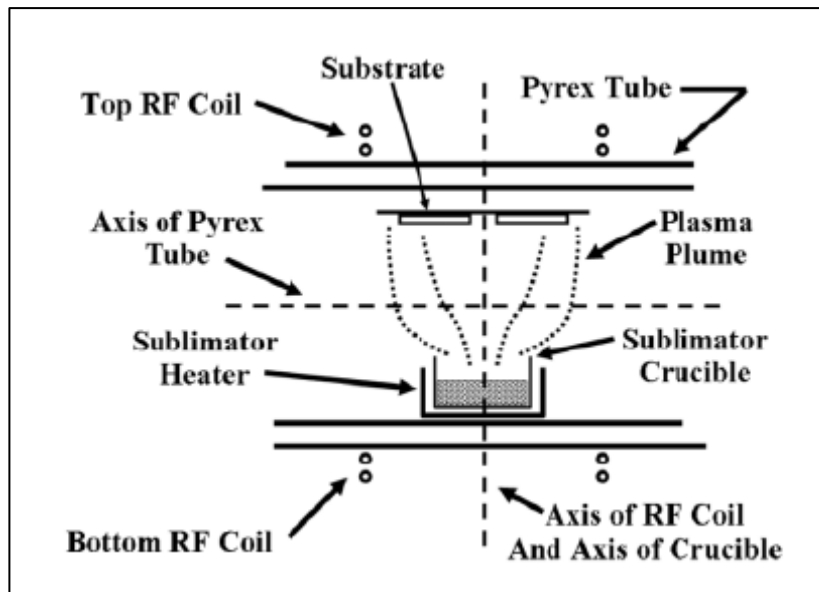


Figure 2.6 Plasma-Enhanced Metalorganic Chemical Vapor Deposition system (Dhar, 1995).

#### 2.4.2 Molecular Beam Epitaxy (MBE): (Norton, 2004, Hong, 2001, Murphy, 2005).

In this technique, the growth is performed under clean, low pressure conditions where the potential for contamination is minimized. The wafer on which growth occurs is held at an elevated temperature so that arriving Zn and O atoms have sufficient energy to move around on the surface of the wafer and find their correct bonding positions. The source materials for the growth are very pure Zn metal, which is evaporated from an oven toward the wafer, and atomic oxygen derived from plasma or ozone source. MBE is capable of layer – by – layer growth with excellent control of the purity and crystalline quality of the resulting film. Figure 2.7 shows a typical MBE system.

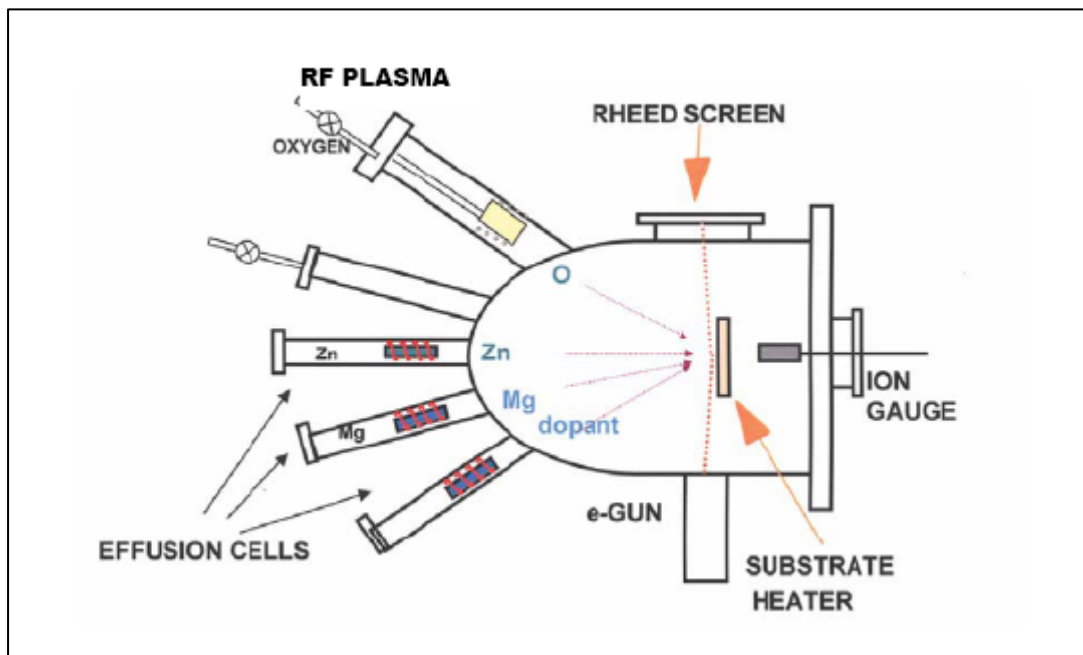


Figure 2.7 Schematic of MBE system (Vispute, 1998).

#### 2.4.3 Pulsed Laser Deposition (PLD): (Vispute, 1998).

A focused laser pulse is directed onto target of material in a vacuum chamber (Figure. 2.8). The laser pulse locally heats and vaporizes the target surface, producing an ejected plasma or plume of atoms, ions, and molecules. The plume of material is deposited onto an adjacent substrate to produce a crystalline film. This technique possesses several favorable characteristics for growth of multicomponent materials, such as stoichiometric transfer of the target material to the substrate, compatibility with a background gas, and atomic level control of the deposition rate. In this method, oxidation of Zn primarily occurs in the ZnO ablation plasma plume, thus alleviating the difficulties encountered with MBE of ZnO, where oxidation proceeds via surface reactions.

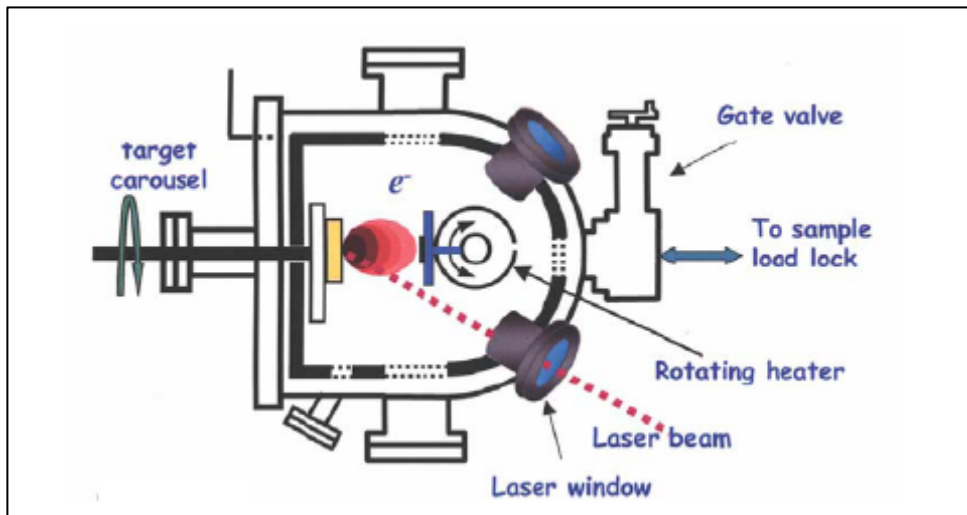


Figure 2.8 Schematic of PLD system (Norton, 2004).

2.4.4 *Spray Pyrolysis Deposition (SPD)*: (Okuya, 2004, Pushparajaht, 1994, Afify, 2005).

Because the film formation is carried out in air by a simple apparatus in SPD, the technique is one of the most attractive film preparation methods. SPD is essentially the same film processing technique as so-called pyrosol technique, in which a source solution is sprayed on the heated substrate, where a film is deposited (see Figure 2.9). In other words, when a source solution is atomized, small droplets splash and vaporizes on the substrate and leaves a dry precipitate in which thermal decomposition occurs. Organometallic compounds such as lithium, copper, and magnesium are used as source materials as well as zinc which are dissolved in water, ethanol, or other solvents to prepare source solutions. Since the source materials dissolve in a solvent as an ion, oligomer, or cluster depending on their chemical properties, the surface morphology of deposited films is easily controlled by choosing species of the source materials.



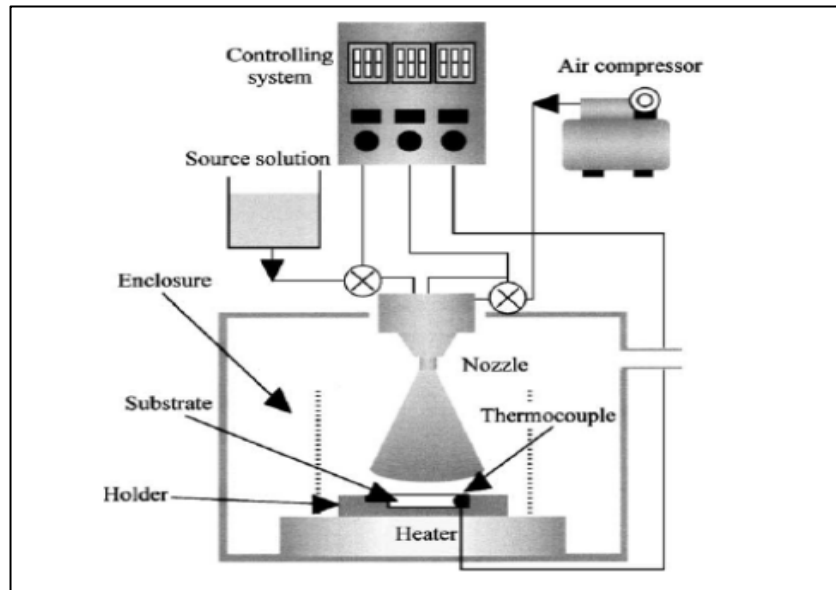


Figure 2.9 Schematic representation of a spray pyrolysis deposition (SPD) (Okuya, 2004).

#### 2.4.5 Magnetron Sputtering: (Kim, 1997, Yeom, 1989, Bose, 1996, Cebulla, 1998).

The planar magnetron sputtering source was invented at the beginning of the seventies (Ellmer, 2000). This technique is now one of the most versatile used for the deposition of transparent conducting oxides (TCO). The fundamental difference between magnetron sputtering as a plasma process and thermally excited thin-film preparation methods (evaporation, chemical deposition methods) is the much higher energy input into the growing film that can be achieved by magnetron sputtering. This technique is characterized by the following advantages such as low substrate temperature, good adhesion of films on substrates, high deposition rates (up to  $12 \mu\text{m min}^{-1}$ ), very good thickness uniformity and high density of the films, good controllability and long-term stability of the process, able of forming many compounds from elemental (metallic) targets and relatively cheap deposition method (Ellmer, 2000). The magnetron sputtering was used in the present work and a general discussion on the principles of magnetron sputtering will be presented.

## **2.5 Sputtering theory**

Many methods can be used to deposit metallic thin films. The two most common methods are evaporation and sputtering. Evaporation is performed by simply placing the metal to be evaporated into a bowl. The substrate on which the film is to be deposited is placed at a desired distance from the bowl. The closer the substrate to the bowl, the faster a thin film will grow on the substrate. The metal is heated under vacuum until it melts and evaporates onto the substrate. Anything in the line of sight of the target will be coated with the evaporated metal.

The basic feature of a magnetron discharge is the confinement of the plasma in front of the target. This is achieved by the combination of electric and magnetic fields (Bunn, 1935). In standard sputtering processes, there are usually two modes of powering the magnetron sputtering system. These two modes are direct current (DC) magnetron sputtering or by radio frequency (RF) magnetron sputtering. In DC magnetron sputtering, a direct voltage is applied between the cathode and anode. This method works well with conductive targets (zinc, molybdenum, silver, aluminum, etc). This mode was mainly employed in the present study.

Sputtering is a removal of surface atoms due to particle bombardment which is caused by atomic collisions at the surface of a target. The process was first reported by Grove (1853), who observed metallic deposition within a discharge tube. The sputtering process is no longer an unwanted effect destroying cathodes or contaminating plasmas, but is nowadays a widely used method for surface cleaning and deposition of thin films and functional coatings.

The material to be deposited (target) acts as the cathode and is connected to a negative voltage supply which could be either DC or RF. The substrate is placed on a substrate holder and could be grounded, floating, biased, heated, cooled, or could

be a combination of these. The substrates are placed exactly above the target. This setup is placed inside a vacuum system which is pumped down and maintained at high vacuum. An inert gas like argon is introduced into the system as the medium for glow discharge. This is because an inert gas like argon has its metastable energy greater than its first ionization potential which helps in producing a sufficient supply of ions for self sputtering. When this glow discharge is initiated, ions with high kinetic energy strike the cathode and the subsequent collisions knock loose the neutral atoms from the material by momentum transfer. These neutral atoms then condense on the substrate to form thin films. The principle of momentum transfer used to deposit materials has made the sputtering technique very attractive and shown in figure 2.10. Using this technique it is easy to deposit materials which could not be easily deposited using other techniques.

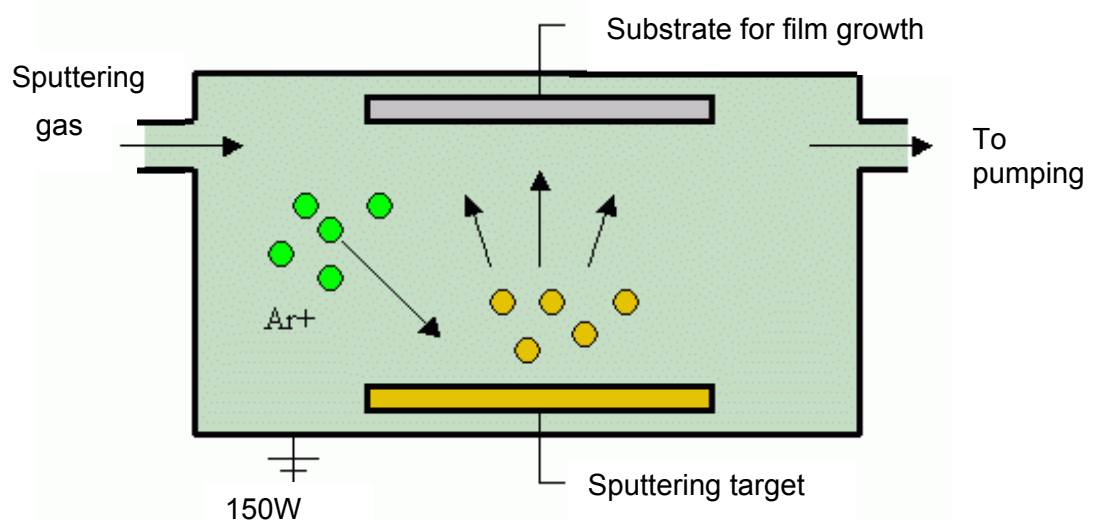


Figure 2.10 A sputtering technique used to deposit thin films of a material onto a substrate ([http://en.wikipedia.org/wiki/Sputter\\_deposition](http://en.wikipedia.org/wiki/Sputter_deposition)).

Although the glow discharge sputtering technique seems to be a powerful deposition technique, the major disadvantage of this technique is its low ionization efficiency. In the case of magnetron sputtering, the ionization efficiency is improved

by using a magnetic field parallel to the cathode surface and thus restraining the primary electron motion to the vicinity of the cathode. These trapped electrons thus move inside the orbit and gain a higher mean free path and collisionally scattered before reaching the anode. Consequently, magnetron sputtering requires lower gas pressures to sustain the plasma as compared to that of the diode sputtering technique. Reduced scattering and increased electron usage efficiency leads to a better deposition rate and reduced applied voltage to sustain plasma in this technique.

## **2.6 Metal-semiconductor contact**

The metal-semiconductor contact or metal-semiconductor junction is undeniably an essential part of all semiconductor devices. In order to form a reliable and a quality device, an ideal or a high quality metal-semiconductor junction must be formed according to the design requirements of the device. Moreover, many of the useful properties of a p-n junction can be achieved by simply forming an appropriate metal-semiconductor contact. Basically, metal-semiconductor contacts can be categorized into two types: the rectifying metal-semiconductor contact, which is equivalent to a p-n junction diode and the non-rectifying (ohmic) metal-semiconductor contact. This metal-semiconductor contact play an important role in all the semiconductor devices particularly when high-speed rectification is required and are very attractive due to their fabrication simplicity.

In ideal metal-semiconductor contact theory, a metal-semiconductor junction may form an ohmic contact or rectifying contact as shown in figure 2.11.

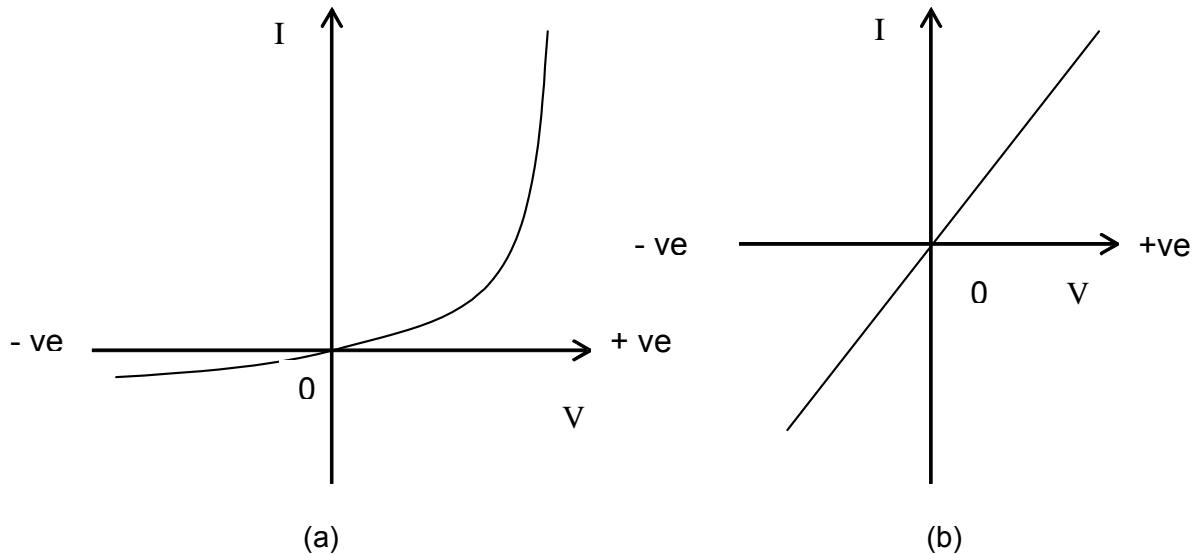


Figure 2.11 Rectifying (a) and linear or ohmic (b) I – V characteristics of metal semiconductor interface.

In many cases we wish to have an ohmic metal-semiconductor contact, having a linear I-V characteristics in both biasing directions either in forward bias (positive bias to the p-type semiconductor) or a reverse bias (positive bias to the metal). For example, the surface of a typical integrated circuit is a maze of p and regions, which must be connected and interconnected. It is important that such contacts be ohmic, with minimal resistance and no tendency to rectify signals.

## 2.7 Current state of research in ZnO

In past years, many researchers have investigated thin film fabrication processes of ZnO. In most ZnO devices, the crystalline quality of the film is a key property. For example, ZnO films should have highly c-axis preferred orientation for application of longitudinal bulk wave transducers and SAW filters (Lee, 1998). The crystalline quality, in particular the preferred orientation, depends on sputtering parameters and the nature of the substrate. Under optimized conditions, the c-axis orientation is frequently observed in sputtered polycrystalline films even on a glass substrate. This is reasonably understood since the c-plane of the ZnO crystallites corresponds to the

densest packed plane. Sputtering has proven to be a successful method of coating a variety of substrates with ZnO thin films for applications in piezoelectric transducers, photoconductors and photonic.

Among possible dopants, nitrogen appears to be a more promising choice than other impurities since it is a known p-type dopant for ZnSe. Acceptor concentrations as high as  $10^{18} \text{ cm}^{-3}$  were obtained in ZnSe samples grown by molecular beam epitaxy (MBE) using nitrogen atom beam doping (Park, 1990). An early N-doped, p-type ZnO result was reported by Minegishi (1997). The p-type ZnO films were grown by chemical vapor deposition (CVD) from a ZnO source powder with excess Zn onto a heated (650 – 800 °C) sapphire substrate. The N source was  $\text{NH}_3$  carried by purified hydrogen gas, which is introduced during deposition. The resulting ZnO films had hole concentrations up to  $1.5 \times 10^{16} \text{ cm}^{-3}$  and a resistivity of about 100  $\Omega \cdot \text{cm}$ .

One problem with N-doping is the low solubility of nitrogen in ZnO (Lee, 2001). Yamamoto (1999) proposed that the solubility of nitrogen can be increased by introducing group III codopant such as Al, Ga or In. Yamamoto calculations showed that reactive codopants such as Al, Ga and In could form complexes with nitrogen, which enhance the incorporation of N-acceptors and thus produce p-type ZnO (Yamamoto, 1999). Joseph (1999) reported p-type results by codoping ZnO with Ga and N.

Sieber (1998) reported the microscopic characterization of reactively sputtered ZnO films with different Al-doping levels using co-sputtering from separate Zn and Al targets. At low Al concentration, typical columnar structure was observed. As the Al doping level increased, fine crystallites appeared on the substrate surface and columnar grains started growing onto them. Finally, the structure of ZnO films was changed to fine