SYNTHESIS AND CHARACTERIZATION OF SILVER DOPED ZINC OXIDE THIN FILMS FOR OPTOELECTRONIC DEVICES

By

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To my future wife and kids
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The synthesis and properties of Ag-doped ZnO thin films were examined. Epitaxial films of 0.6 at.% Ag doped ZnO grown at moderately low temperatures (300 °C to 500 °C) by pulsed laser deposition yielded p-type material as determined by room temperature Hall measurements. Carrier (hole) concentrations ranging on the order mid-10^{15} \text{cm}^{-3} to mid-10^{19} \text{cm}^{-3} were realized. Growth at higher temperatures yielded n-type material, suggesting that the Ag substitution yielding an acceptor state is metastable. Photoluminescence measurements showed strong near-band edge emission with little to no mid-gap emission. The stability of the Ag-doped films was examined as well. Persistent photoconductivity was observed. ZnO buffer layers drastically improved the surface morphology of films thicker than 1.0 \mu m.

Photoluminescence studies showed that Ag inclusion resulted in smaller non-radiative relaxation rates over surface states, which lead to UV emission enhancement. Room temperature PL measurements also showed a suppression of ZnO visible luminescence suggesting that Ag does not occupy interstitial sites or an antisite. Low temperature and temperature dependent PL spectroscopy revealed strong and
dominant emissions originating from free electron recombination to Ag-related acceptor states around 3.31eV. The AºX emission at 3.352 eV was also observed at low temperatures. Enhancement of the PL intensity with increasing grain size was observed. The nature of the acceptor related emissions was confirmed. The acceptor energy was estimated to be 124 meV. Weak deep level emission at low temperatures indicated that in the p-type ZnO:Ag native donor and acceptor defects are suppressed suggesting the observed acceptor related PL emissions and hole concentration are from the Ag in ZnO instead of native defects. High temperature ZnO buffers and lattice matched MgCaO buffers helped improve the UV emission of the Ag doped films. The room temperature PL spectrum of Ag-doped ZnO was compared to that of undoped, P-doped, Ga-doped, and Ag-Ga- codoped ZnO. The Ag-doped ZnO films showed superior optical properties.

Finally, the fabrication and properties of rectifying Ag-doped ZnO/Ga-doped ZnO thin film junctions were reported. A rectifying behavior was observed in the I-V characteristic, consistent with Ag-doped ZnO being p-type and forming a p-n junction. The turn on voltage of the device was 3.0 V under forward bias. The reverse bias breakdown voltage was approximately 5.5 V. The highest light emission output power measured was 5.2x10^-8 mW. At excitation currents of 10 mA, the applied voltage was approximately 2.0 V. After each measurement the light intensity decreased and the junction became Ohmic. The instability appears to be related to surface conduction and perhaps hydrogen incorporation. Finally, deposition of layers in reversed order (Ag-doped ZnO on bottom, Ga-doped ZnO on top) did not result in rectifying I-V
characteristics. The reason for this is unclear but may relate to the differing growth temperatures used for the two layers.
In recent years, the market of electronic devices that source, detect, and control light has grown rapidly. Light emitting diodes (LEDs) and laser advancements have significantly contributed to this rapid growth. Nitride-based devices, in particular, have entered the communication, display, traffic signal, and automotive industry. In the near future, white LEDs are expected to develop as a major market replacing incandescent and fluorescent lamps in general lighting applications.

The GaN semiconductor system has dominated the solid-state lighting field for approximately two decades. The need for short-wavelength photonic devices, high power, and high-frequency electronic devices in addition to the high quality synthesis of GaN has established its dominance. ZnO, however, has gained substantial interest in part because of its advantages over GaN and thus is considered an alternative material.

Initially, ZnO was studied for its polycrystalline properties and applications to facial powders, varistors, piezoelectric transducers, and transparent conductive films. Lately, however, large area bulk ZnO growth has been achieved [1], and epitaxial thin film growth optimized [2]. Hence, the motivation for renewed focus on ZnO photonics research. ZnO has several advantages over GaN:

- ZnO has an exciton binding energy of 60 meV, while that of GaN is only 26 meV. This large binding energy is of particular interest because its excitonic emission may be used to obtain lasing action above room temperature [3].

- ZnO is available in large area bulk wafers while no bulk wafers are available for GaN. Single-crystal growth by seed vapor phase (SVP) is the method used to fabricate commercially available 2-inch wafers [4]. High quality homo-epitaxial ZnO growth is possible using these native substrates. Thus, concentrations of dislocations and point defects due to lattice mismatch are relatively low in ZnO films compare to GaN [5].
• Highly resistant to ion-beam-induced build-up damage. ZnO retains its crystallinity even after heavy-ion bombardment and exhibits no defect saturation in its crystal bulk [6]. Such radiation resistance makes ZnO a fitting candidate for space and harsh environment applications.

• Wet chemical etch processing is possible. Wet etching processing is extremely important in device fabrication because it provides lower costs and relative ease of processing.

In addition, ZnO exhibits a direct wide bandgap of 3.37 eV at room temperature. Mg$_x$Zn$_{1-x}$O and Cd$_x$Zn$_{1-x}$O ternary alloys are used to fabricate multiple quantum wells (MQW) structures. The bandgap can be varied from 3.0 to 4.0 eV using such alloys without changing ZnO wurtzite structure [7, 8]. Such bandgap tuning makes possible the fabrication of heterojunction structures for lasers and LEDs.

Both n-type and p-type ZnO are required for the development of homojunction LEDs and laser diodes. Although strong n-type ZnO is easy to obtain, reliable, high conductivity p-type ZnO still remains a major challenge. Substitution of N for O has been the focus of most efforts in obtaining p-type ZnO. Also, P and As, albeit their large size compare to O, have been widely used to obtain p-type conductivity. Compensating defects such as Oxygen vacancies (V$_{O}$) and Zinc interstitials (Zn$_i$), and relatively large energies necessary to create unfilled states in the deep valence band, however, still remain an issue in attaining robust p-type [9]. Therefore, reducing the background compensating defect density and fabrication of high quality films is fundamental in obtaining robust p-type conductivity.

Silver, a rather limited studied, group IB element, is expected to favorably substitute Zn yielding a shallow acceptor state [10]. Unlike other group I elements, namely Li, Na, or K, Ag is expected to easily incorporate on the Zn site rather than occupy interstitial sites [11, 12]. The focus of this study was to address the effects of Ag
doping on ZnO thin film properties grown by pulsed laser deposition (PLD). In addition, it addresses the fabrication of rectifying junctions, and p-MOS devices.
CHAPTER 2
LITERATURE REVIEW

2.1 General Properties of ZnO

At ambient conditions, ZnO exhibits a hexagonal wurtzite structure with a tetrahedral coordination typical of $sp^3$ covalent bonding, but has considerable ionic character. Although the wurtzite structure is thermodynamically stable at ambient conditions, a zinc-blende structure may be obtained when grown on cubic substrates, while rocksalt (NaCl) when grown at high pressures. The lattice parameter of wurtzite ZnO are $a = 3.2495$ Å and $c = 5.2069$ Å [13]. The unit cell is composed of two interpenetrating hexagonal-closed-packed (HCP) sublattices, where each Zn atom is surrounded by four O atoms in a tetrahedral coordination, and vice versa. There is a deviation from the ideal wurtzite crystal due to lattice expansions and ionicity [3]. Lattice expansions are attributed to free charges, point defects, and threading dislocations. Thus, undoped ZnO is typically non-stoichiometric and shows n-type conductivity. The ionic radii are 0.60 Å and 1.38 Å for $\text{Zn}^{2+}$ and $\text{O}^{2-}$, respectively. Figure 2-1 shows the hexagonal wurtzite structure of ZnO.

The wurtzite ZnO conduction band is made of an $s$-like state having $\Gamma_7$ symmetry. Its valence band is made of a $p$-like state, which splits into three bands due to crystal field and spin orbit interactions [14]. ZnO exhibits a direct and large bandgap, which allows it to sustain large electric fields and higher breakdown voltages. In addition, lower noise generating, high temperature, high power devices can be fabricated.

2.2 Doping of ZnO

ZnO, a II-VI semiconductor, emits light in the near-UV region of the spectrum. The semiconductor large exciton binding energy (60 meV), has enabled room temperature
lasing and stimulated emission at temperature up to 550 K, establishing ZnO as an interesting photonic semiconducting oxide [5]. The synthesis of heavily doped n-type ZnO is easily accomplished via group III cation doping. However, the control over dopants and defects that may lead to high quality and robust p-type still remains a major challenge to the fabrication of practical devices.

2.2.1 Undoped ZnO and Its Native Defects

Undoped ZnO normally exhibits n-type conductivity. The role of native defects such as vacancies \(V_O\) and \(V_{Zn}\), interstitials \(Zn_i\) and \(O_i\), and antisites \(Zn_O\) and \(O_{Zn}\) in undoped ZnO is not yet clearly understood. Several studies [15-17] claim that such native defects create shallow donor states. D.C. Look et al. suggested that \(Zn_i\) rather than \(V_O\) are the main cause for n-type conductivity, acting like shallow donors, in ZnO [18]. However, more recent theoretical and experimental studies [19-24] argue that \(Zn_i\) are unstable and diffuse at room temperature, while \(V_O\) are deep compensating defects not responsible for the n-type material. These studies suggest that hydrogen and group III elements impurities are more likely to be responsible for the intrinsic conductivity in ZnO.

Theoretical work by Van de Walle [25] showed that interstitial H is a shallow donor in ZnO. This was confirmed by experimental results [26] that showed a three orders of magnitude increase in conductivity in ZnO films when grown in \(H_2\) by pulsed laser deposition (PLD). Secondary ion mass spectroscopy (SIMS) analysis revealed Ca-H complexes, where Ca donates an electric charge to a neighboring O atom that traps a H atom, allowing it to act as a shallow donor. Another first principle study [27] demonstrated that H can substitute an O atom and act as a shallow donor as well.
Unlike interstitial H, substitutional H is stable and has a high migration energy, thus, making it a strong candidate for H-related donors in as-grown ZnO [28].

In order to efficiently dope and fully exploit the intrinsic properties of ZnO, the effects of each of these native defects must first be fully understood and controlled.

2.2.2 N-type Doping

ZnO is easily doped n-type by cation substitution using group III elements or anion substitution using group VII elements. The most frequently used dopants are Al, Ga, and In, which have resulted in high quality, and highly conductive films. Myong et al. [29] and Ataev et al. [30] reported resistivities as low as $6.2 \times 10^{-4}$ and $1.2 \times 10^{-4}$ $\Omega\cdot$cm for ZnO films doped with Al and Ga, respectively. Films with carrier concentrations of up to $10^{21}$ cm$^{-3}$ have been realized, which have led to their use as n-type layers for LEDs and transparent Ohmic contacts.

2.2.3 P-type Doping

It is well known that n-type ZnO is easily fabricated, while p-type still remains a major obstacle. This is common in wide bandgap semiconductor because of the low formation energies for compensating defects.

Candidates for p-type doping include group V anions on oxygen sites or group I or IB cations on Zinc sites. Most research efforts have focused on group V dopants, namely, N [31, 32], As [33, 34], P [35-37], and Sb [38]. First principle calculations [39, 40], predicted that group I elements are shallow acceptor, while group V elements, for the most part, are deep acceptors. C.H. Park et al. calculated defect energy levels relative to the valance band maximum (VBM) for each cation and anion substitution. The results are summarized in table 2-1. The VBM is made of anion p-orbitals with small mixing of cation p-d orbitals. Therefore, group I doping results in smaller
perturbation and shallower defects than group V doping. However, group I elements rather occupy interstitial sites [11, 40] mitigated by their small size. Both P and As have significantly larger bond length and therefore are more likely to form antisites to avoid lattice strains. Theoretically, N is favored among group V elements because it has a similar bond length to ZnO, low ionization energy, and unlikely antisite formation (N\text{Zn}) [40].

**Nitrogen Doping**

As mentioned above, N is the most promising candidate for p-type ZnO and a good deal of effort has been focused in using it as a shallow acceptor dopant. Several studies [41-43] have been devoted to find the right source for Nitrogen doping during film growth. X. Li *et al.* [41] reported p-type conductivity, with carrier concentrations ranging from $10^{15}$ to $10^{18}$ cm$^{-3}$, using NO as its dopant source. W. Xu *et al.* [43], using both NO and N$_2$O, obtained similar carrier concentrations and resistivities as low as 3.02 $\Omega$-cm. Z.-Z. Ye *et al.* [44] grew p-type films using NH$_3$-O$_2$ and obtained carrier concentrations of 3.2x$10^{17}$ cm$^{-3}$ and 1.8 cm$^2$V$^{-1}$s$^{-1}$ mobilities.

Oxygen-poor growth conditions are required to incorporate dopants into O sites, which promotes “hole killer” defects and compensation [39, 45-47]. The low solubility of N is well known. Only about 0.1 % of the dopant seems to be electrically active, while the remaining inactive N acts as scattering centers resulting in low carrier mobility [45]. In order to increase the N solubility, codoping methods have been engineered using reactive donor dopants such as Ga, Al, and In. N-codoping lowers the acceptor level in the bandgap due to strong interaction between acceptors and donors codopants [3]. SIMS results showed an increase of N-solubility by a factor of 400 when using Ga as
the reactive donor codopants. Furthermore, M. Joseph *et al.* [48], using N-Ga codoping via pulsed laser deposition (PLD), successfully grew p-type films. For these films the hole concentration was $4 \times 10^{19}$ cm$^{-3}$ with 2.0 $\Omega$-cm resistivity. However, the carrier mobility did not improve. Sing *et al.* [49], showed a relation between $V_{O}$, oxygen partial pressure and carrier type. Results showed that at ratios of oxygen partial pressure to total pressure ($4 \times 10^{-4}$ Torr) below 40% films were n-type, while films grown at ratios above 50% showed p-type conductivity. Further increase of pressure, above ratios of 60%, resulted in high resistivities and low mobilities due to crystal degradation by oxygen related defects. P-type ZnO was also achieved using Al [50] and In [51] as codopants, however, high carrier concentrations and incredibly high (~150 cm$^{2}$V$^{-1}$s$^{-1}$) mobilities bring the validity of the results into question. In other studies [52-54], despite achieving high concentration of N incorporation, codoping yielded only n-type ZnO.

**Other group V Dopants**

Fewer studies [55-63] have considered other group V elements for substitutional doping. Based on theoretical calculations, both P and As are predicted to be deep acceptors and carrier type inversion rather difficult to achieve. Other compensating defects, such as antisites, AX centers and $V_{Zn}$, are expected to be stable due to larger bond lengths and lattice strain relaxation. Despite theoretical predictions, several groups [55, 61, 64] have reported p-type ZnO. Aoki *et al.* [57], realized p-type ZnO by diffusing P into ZnO substrates via laser irradiation of Zn$_3$P$_2$. Kim *et al.* [55], achieved carrier type conversion via rapid thermal annealing (RTA) of n-type ZnO:P films. Other groups [60-62] used As, while Xiu *et al.* [63] used Sb as p-type dopant. Furthermore,
Capacitance-Voltage (CV) measurements showed that Zn_{0.9}Mg_{0.1}O can be made p-type using P_2O_5 as the phosphorus source, but p-type ZnO was not achieved [59].

The lack of reproducibility, carrier type changes and lattice constant relaxation over time has raised doubts about the validity of the reports of p-type ZnO. In addition, the apparent p-type conductivity may be the result of interface and near-surface states [64] and/or inhomogeneous samples [65]. Therefore, a better understanding of the physical properties of point defects may be useful.

**Silver Doping**

In comparison to the group V elements, studies on group IB dopants, namely Cu or Ag, in ZnO have been rather limited [66-68]. Early reports argued that Ag substitution in ZnO forms a deep acceptor state 0.23 eV below the bottom of the conduction band [10]. However, recent studies suggest this may not to be the case. One study reported an acceptor state binding energy for the Ag 3d^{10} states of only 200 meV [69]. Another study of the behavior of Ag in bulk ZnO suggests that Ag acts as an amphoteric dopant, yielding an acceptor state for substitution on the Zn site, and a donor state for interstitial defects [70]. First-principles calculations have examined the dopant energy levels and defect formation energies for group IB elements in ZnO [66]. The calculations estimate the acceptor state ionization energies for substitutional Ag, Cu, and Au to be 0.4, 0.7, 0.5 eV, respectively. Although these represent relatively high ionization energies, the formation energies for these substitutional defects (Cu_{Zn}, Ag_{Zn}, and Au_{Zn}) are predicted to be low; energies for interstitial defects are predicted to be high. These calculations suggest that solubility and self-compensation may be less of an issue for group IB elements as compared to the group V dopants.
Within the group IB elements, Ag has the lowest predicted transition energy (0.4 eV) [66], reflecting a weaker $p$-$d$ orbital repulsion as compared to Cu or Au. This weak repulsion is rooted in the large size and low atomic $d$-orbital energy of Ag. Interestingly, the O-rich conditions that have been suggested for preventing oxygen vacancy ($V_O$) and/or Zn interstitial ($Zn_i$) defects are consistent with the required conditions for substituting Ag onto the Zn site. A few groups have experimentally examined the properties of Ag-doped ZnO. H. S. Kang et al. have reported the formation of p-type ZnO via Ag doping in thin films grown by pulsed laser deposition [71]. The formation of p-type material was limited to deposition temperatures of 200-250ºC. Studies on Ag-implanted ZnO suggest that Ag substitution on the Zn site becomes unstable at temperatures greater than 600ºC [72]. This is consistent with the estimated 0.08 mol% bulk solid solubility of Ag in ZnO [73].

2.3 ZnO Band-Gap Engineering and Devices

As mentioned before, p-type ZnO must be accomplished in order to fabricate practical devices and therefore the vast majority of research has been dedicated to its realization. However, another important step in realizing ZnO based optoelectronic devices is bandgap modulation and indeed it has been demonstrated by Mg [74-79] and Cd [80-86] alloying.

2.3.1 Bandgap Engineering

The band-gap energy of a ternary alloy $AxZn_{1-x}O$ (where $A = Mg$ or Cd) is given by the following equation [87]:

$$E_g(x) = (1-x)E_{ZnO} + xE_{AO} - bx(1-x)$$  \hspace{1cm} (1)

Where $b$ is the bowing parameter and $E_{AO}$ and $E_{ZnO}$ are the band-gap energies of compounds AO and ZnO, Respectively.
Figure 2-2 shows the bandgap and lattice constant of various semiconductors. Band-gap modulation can be achieved by alloying ZnO with MgO (Eg ~7.7 eV) in order to increases the band-gap ZnO. On the other hand, alloying with CdO (Eg ~ 2.3 eV) results in a decrease of the band-gap. Ohtomo et al. [74] found a linear relation between Mg content and band-gap up to about 3.9 eV. This band-gap value corresponds to a Mg content of 0.33, above which segregation of MgO is observed. The properties of ZnO-ZnMgO quantum well structures were also studied and quantization behavior and increased exciton binding energy (E_b > 96 meV) were observed [77]. Similarly, Makino et al. [86] found that the band-gap of ZnO can be decreased from 3.28 to 2.99 eV with Cd content of 7% and estimated a non-linear band-gap to content relation 

\[ E_g(y) = 3.29 - 4.40y + 5.93y^2. \]

XRD studies also showed that the unit cell volume increased, as both lattice parameter (a and c), increased with Cd content.

2.3.2 ZnO Devices

To reiterate, the realization of reproducible, high quality p-type ZnO has been the bottleneck of ZnO device processing. Despite this difficulty, ZnO based homojunction devices have been fabricated [88-90]. However, most efforts have been focused on the making of p-n heterostructure devices using ZnO as the n-type layer [90-102].

ZnO homojunction devices

Recently, Liang et al. [88] deposited undoped ZnO films on heavily P-doped n+ Si substrate via metal organic chemical vapor deposition (MOCVD). Upon diffusion of P, from the Si substrate into the ZnO film, a ZnO:P/ ZnO junction was formed. Current-voltage (I-V) characteristics showed good rectifying behavior with a turn on voltage of 4.2 V under forward bias and a reverse breakdown voltage of about 6 V. No electro-
luminescence (EL) was observed under reverse bias; however, the blue-white light under forward bias was clearly seen even with naked eyes in the dark. EL and PL measurements from the ZnO-based device are shown in Figure 2-3. Similar results were obtained for ZnO films deposited on GaAs substrate [89]. Arsenic diffused from GaAs substrate was used to dope ZnO p-type, while ZnO:Al was used as the n-type layer. EL measurements revealed an emission peak centered at ~ 2.5 eV and a weaker shoulder at ~ 3.0 eV. Later, Sun et al. [90] reported EL emissions centered at 3.2 and 2.4 eV under forward biased for films doped with N and Ga as p-type and n-type dopants, respectively. EL spectrum of the device under a direct forward bias current of 40 mA at room temperature, and IV characteristics is shown in Figure 2-4. The UV emission reported was comparable with the visible emission in the EL spectrum, which is a significant step forward in the performance of ZnO homojunction LEDs.

**ZnO heterostructure devices**

In the absence of reliable p-type ZnO, research groups, in an effort to exploit ZnO many advantages, have spent a great deal of attention making heterostructure devices. When Sun et al [90] used Cu$_2$O and ZnO substrate as p and n layers respectively, measurements revealed EL in both forward and reverse biases. Later, Tsurkan et al. [91] used p-type ZnTe on n-ZnO substrates varying carrier concentrations for each layer. Although, strong EL emissions were observed for all carrier concentrations under forward bias, the EL spectrum was dominated by different emission bands as the result of carrier diffusion from low to high resistive layers. Other materials such as Si [92], GaN [93], AlGaN [94], SrCu$_2$O$_2$ [95], NiO [96], CdTe [97], and SiC [98] have been used with n-type ZnO to create useful heterostructure devices.
The structural relationship between the materials forming the junction is an important factor in realizing high-quality heterostructure devices, because the lattice-mismatch between them causes defects that act as nonradiative centers and lowers the device efficiency. For this reason, using p-GaN (1.8% mismatch with ZnO) and n-ZnO is promising. Alivov et al. [93] fabricated p-GaN/n-ZnO junctions. The observed EL emission, under forward bias, was likely to emerge from the p-GaN since band alignment favors carrier injection from n-ZnO into p-GaN. Figure 2-5 shows the EL spectrum of the n-ZnO/p-GaN heterostructure and the broad band emission centered at 430 nm is seen. Subsequently, Al_{0.12}Ga_{0.88}N was used in order achieve carrier injection into ZnO [94] and UV (389 nm) emissions attributed to excitonic recombination in ZnO, were observed (see Figure 2-6). Furthermore, Alivov et al. [99] fabricated laser diodes (LD) by growing n-GaN/n-ZnO/p-GaN structures, thus achieving carrier confinement. I-V characteristics revealed low leakage current and a reverse breakdown voltage of 12 V, while strong EL emissions were also reported.

Photodiodes using n-ZnO layers have been realized as well [98,100-102]. P-type materials employed in their fabrication include p-ZnRh$_2$O$_4$ [102], p-Si [100], p-NiO [96] and p-6H-SiC [98,101]. High-quality diodes that exhibit good photosensitivity to UV radiation and a photoresponse as high as 0.045 A/W at -7.5 V reversed bias have been reported [98,101] using p-SiC. Results are shown in Figure 2-7.

**ZnO Based Thin Film Transistors**

The combination of transparency in the visible, excellent transistor characteristics, and low temperature processing makes ZnO thin-film transistors (TFTs) attractive for flexible electronics on temperature sensitive substrates. Garcia et.al [103], demonstrated the fabrication of transparent ZnO TFTs by RF magnetron sputtering near
room temperatures using n-type Si substrates and 100 nm thick ZnO. High field effect mobilities of 1.2 cm$^2$/Vs and $I_{on}/I_{off}$ ratio of $1.6 \times 10^6$ with drain current greater than $10^{-5}$ A was achieved. The charge accumulation transistor curves are shown in Figure 2-8.

Masuda et al. [104], succeeded at fabricating ZnO TFTs by pulsed laser deposition on glass substrates. A double layer insulator (SiO$_2$ + SiN$_x$) was used to obtain an $I_{on}/I_{off}$ ratio of $10^5$ and an optical visible transmittance of more than 80%. The transistor curves for the double insulator TFTs are shown in Figure 2-9.

Many other studies [105-112] have reported successful fabrication of ZnO TFTs grown at both low and room temperature in a variety of substrates such as amorphous glasses, plastics or metal foil. More reliable and efficient ZnO TFTs are expected to be fabricated in the near future, making invisible electronics possible.
### Table 2-1. Calculated defect energy level for group I and V dopants

<table>
<thead>
<tr>
<th>Defect</th>
<th>Defect energy level (eV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I</td>
<td></td>
</tr>
<tr>
<td>Li&lt;sub&gt;Zn&lt;/sub&gt;</td>
<td>0.09</td>
</tr>
<tr>
<td>Na&lt;sub&gt;Zn&lt;/sub&gt;</td>
<td>0.17</td>
</tr>
<tr>
<td>K&lt;sub&gt;Zn&lt;/sub&gt;</td>
<td>0.32</td>
</tr>
<tr>
<td>Group V</td>
<td></td>
</tr>
<tr>
<td>N&lt;sub&gt;O&lt;/sub&gt;</td>
<td>0.40</td>
</tr>
<tr>
<td>P&lt;sub&gt;O&lt;/sub&gt;</td>
<td>0.93</td>
</tr>
<tr>
<td>As&lt;sub&gt;O&lt;/sub&gt;</td>
<td>1.15</td>
</tr>
</tbody>
</table>

*Relative to valance band maximum (VBM)
Figure 2-1. Wurtzite structure of ZnO

Figure 2-2. Bandgap and lattice constant of various semiconductors

Figure 2-5. EL spectrum of an n-ZnO/p-GaN heterostructure. Reprinted with permission from Figure 4 of Y. I. Alivov, J. E. Van Nostrand, D. C. Look, M. V. Chukichev, and B. M. Ataev, Appl. Phys. Lett. 83, (2003) 2943.

Figure 2-6. EL spectra of n-ZnO/ p-Al0.12Ga0.88N heterostructure LED at 300 K and 500 K. Reprinted with permission from Figure 4 of Y. I. Alivov, E. V. Kalinina, A. E. Cherenkov, D. C. Look, B. M. Ataev, A. K. Omaev, M. V. Chukichev, and D. M. Bagnall, Appl. Phys. Lett. 83, (2003) 4719.
Figure 2-7. Room temperature spectral photoresponsivity of the n-ZnO/p-SiC photodiode illuminated both from the ZnO and 6H-SiC (inset) sides for various reverse biases. Reprinted with permission from Figure 3 of Y. I. Alivov, Ü. Özgür, S. Doğan, D. Johnstone, V. Avrutin, N. Onojima, C. Liu, J. Xie, Q. Fan, and H. Morkoç, Appl. Phys. Lett. 86, (2005) 241108.

Figure 2-8. (a) is a set of transistor curves of drain current ($I_d$) vs source–drain voltage ($V_d$) at gate voltages ($V_g$) between 0 and 50 V for a ZnO TFT. The corresponding transfer characteristic, $I_d$ vs $V_g$ at a fixed $V_d$ equal to 20 V, for the same ZnO TFT is shown in (b). Reprinted with permission from Figure 3 of P. F. Garcia, R. S. McLean, M. H. Reilly, and G. Nunes, Appl. Phys. Lett. 82, (2003) 1117.
Figure 2-9. Electrical characteristics of a two-layer gate insulator ZnO–TFT prepared with a high carrier concentration ZnO layer: (a) Output characteristics and (b) transfer characteristics Reprinted with permission from Figure 9 of S. Masuda, K. Kitamura, Y. Okumura, S. Miyatake, H. Tabata, and T. Kawai, J. Appl. Phys. 93, (2003) 1624.
CHAPTER 3
MATERIALS AND CHARACTERIZATION TECHNIQUES

The synthesis and characterization of Ag-doped ZnO thin films will be discussed in this chapter. Pulsed laser deposition (PLD) was employed to grow films with thickness ranging from 250 nm to 1.0 μm. In order to find optimal doping conditions, oxygen partial pressures (PO\textsubscript{2}), temperature, and doping levels were varied systematically. To better understand the doping effects on electrical properties, Hall-Effect measurements were performed, while the optical properties were studied by photoluminescence (PL) measurements. Scanning Electron Microscopy (SEM), powder and high resolution X-ray diffraction were used to investigate the microstructure of the films. The surface morphology of the films was characterized by Atomic Force Microscopy (AFM).

3.1 Thin Film Synthesis

3.1.1 Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is a common thin film growth technique used in research studies because it allows for growths ranging from 25 °C to 1000 °C in nearly any desirable background gas. It consists of high power energy pulses that evaporate material from a target surface producing a plasma or plume of atoms, ions, and molecules. The ablated material then condenses on a substrate positioned opposite to the ablation target, forming a thin film with the same composition as the target. Figure 3-1 shows a schematic of the PLD system (growth chamber and laser) used in this research. The quality of the films strongly depends on the laser wavelength, structural and chemical composition of the ablation target and background gas, chamber pressure, and substrate temperature and distance to ablation target.
The base pressure of the chamber used for these film growths was approximately $10^{-8}$ Torr. A KrF excimer laser with a 248nm wavelength used was the ablation source with an energy density of about 1.0 J/cm$^2$ at the target surface. The background gas used during all growths was ultra-high purity Oxygen.

3.1.2 Target and Substrate Preparation

Ablation targets were fabricated using ultra high purity ZnO and Ag$_2$O powders. The targets were sintered at 1000 °C in air. The concentrations of Ag in the ZnO targets were 0.75 at%, 0.1 and 0.5wt%. These concentrations of Ag were somewhat arbitrary, made based on some rough assumptions regarding activation energy of the acceptor and desired hole concentration. Single crystal $c$-plane sapphire and ZnO substrates were employed in this study. Substrates were cleaned using supersonic baths in trichloroethylene, acetone, and methanol subsequently. The target to substrate distance was ranged from 3.5 to 6.0 cm.

3.2 Characterization Techniques

3.2.1 Hall Effect Measurement

The Hall effect is widely used in semiconductor research because it permits one to determine the carrier density, mobility and majority carrier type. When a magnetic field is applied perpendicular to the current flow, charge carrier separation occurs resulting in an electrical field perpendicular to both the applied magnetic field and current direction. The potential drop across this electrical field is called the Hall voltage ($V_H$). Figure 3-2 shows a schematic of the Hall effect. The Hall coefficient can also be extracted from Hall effect measurement and can be written as:

$$R_H = \frac{r (p - b^2)}{q (p + bn)^2} = \frac{r_H}{qp} \text{ (for p-type)} \text{ or } R_H = -\frac{r_H}{qn} \text{ (for n-type)}$$

(2)
Where \( b \) and \( r \) are scattering factors, \( n \) and \( p \) are electron and hole density, respectively.

Also, it can be determined experimentally using the \( V_H \)

\[
R_H = \frac{eV_H}{B_l} = \frac{1}{qp} \quad \text{(for p-type)} \quad \text{or} \quad R_H = -\frac{1}{qn} \quad \text{(for n-type)}
\]  

(3)

Where \( B \) is the applied magnetic field, and \( t \) and \( I \) are the thickness and applied current on the sample. Other Hall parameters can be expressed using the following equations.

Mobility: \( \mu_H = \frac{R_H}{\rho} \);  

(4)

Resistivity: \( \rho = \frac{R_{wt}}{L} = \frac{V/I}{L/wt} \)  

(5)

Where \( R \) is the resistance, \( w \) is the sample width, \( L \) is the sample length, and \( V \) is the voltage across the sample.

It should be noted that ZnO is a compensated semiconductor and in this study, in order to reliably delineate the carrier type and density for highly compensated samples, the Hall measurements were performed at various magnetic field values and over a large magnetic field range. Furthermore, the measured transverse voltage is the sum of the Hall voltage, an offset voltage (due to non-ideal contact geometry), magnetoresistance, and noise. Only the Hall voltage should be linearly dependent on applied magnetic field, making the sign of the Hall coefficient easily confirmed from the slope of the measured voltage as a function of applied magnetic field.

3.2.2 Photoluminescence (PL)

Photoluminescence (PL) is a nondestructive technique used to characterize the bandgap, impurity and defect levels in semiconductors. The light source, having greater energy than the bandgap of the semiconductor, is directed to the sample and creates
electron-hole pairs by promoting carriers to allowable excited states. Upon returning to
equilibrium states, the excess energy is released in the form of photons (radiative
process) or phonons (nonradiative process). The energy of the emitted photon is
related to the energy difference between the excited and equilibrium state. For direct
bandgap semiconductors the most common radiative transition is that from the
conduction to the valence band, allowing for bandgap determination. Information about
localized defects and impurity levels can be obtained from the emitted
photoluminescence energy and amount, respectively. There are five common radiative
transitions and are shown in Figure 3-3.

In ZnO, most transitions are only detectable at very low temperatures; therefore,
both room and low (15 K) temperature PL were measured. Moreover, time-resolved PL
measurements were performed to better understand the nature of the defects present in
the Ag-doped ZnO films.

3.2.3 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a technique used to characterize the crystal structure,
size, and preferred orientation in crystalline samples. A beam of X-rays strike a
sample interacting with crystal planes creating a diffraction pattern for constructive
interactions that satisfy Bragg’s Law.

Bragg’s Law: \( n\lambda = 2d \sin \theta \)  

where \( n \) is the order of diffraction, \( \lambda \) is the x-ray wavelength, \( d \) is the interplanar
spacing of crystal planes, and \( \theta \) is the incident angle of x-ray.

In this study, the crystal structure of the films was characterized using high-resolution X-
ray diffraction. The preferred orientation, presence of secondary phases, and lattice
parameter changes were analyzed using the Philips APD3720 system. Information on
crystal quality and symmetry was obtained, from omega and phi scans, using the Philips X’pert high resolution diffractometer.

3.2.4 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a tool used to characterize the surface topology and morphology of thin films. It consists of a cantilever with a sharp tip at its end that is used to scan the sample surface (Figure 3-4). In this research, tapping mode AFM (Digital Instruments Dimension 3100) was employed to map out the topology of the ZnO film surface. In tapping mode, the cantilever oscillates near its resonance frequency. The oscillation amplitude decreases or increases due to interaction of forces acting on the cantilever as the AFM tip comes close the sample surface; thus, imaging the force of the oscillating contacts of the tip with the sample surface.
Figure 3-1. Pulsed laser deposition (PLD) system

Figure 3-2. Hall Effect diagram

$V_H = $ Hall Voltage
$F_M = $ Magnetic Force on electrons
$F_e = $ Electric Force due to charge build up
Figure 3-3. Common radiative transition mechanism

Figure 3-4. Block diagram of atomic force microscope
4.1 Introduction

ZnO is a wide bandgap semiconductor that is attracting significant attention for thin-film electronics [113-115], nanoelectronics [116-118], photonics [119,120], piezoelectrics [121,122] and sensor applications [3,123-125]. The crystal structure of ZnO is wurtzite, with lattice parameters $a = 3.25 \, \text{Å}$ and $c = 5.12 \, \text{Å}$ [126]. ZnO has a direct bandgap of 3.2 eV and a relatively large exciton binding energy of 60 meV. This has enabled room temperature lasing and stimulated emission in the ultraviolet at temperatures up to 550 K, establishing ZnO as an interesting photonic semiconductor oxide [127]. An important issue in developing ZnO-based electronics is the formation of robust p-type material. This is obviously relevant for the fabrication of pn junctions for minority carrier injection [128-130]. It is also important for p-channel thin film transistors [20] as well as in spin-doped ZnO where the ferromagnetic ordering appears linked to carrier density and carrier type [132,133]. Undoped ZnO is normally n-type due to native defects that create shallow donor states [15]. The synthesis of heavily doped n-type ZnO is easily accomplished via group III cation doping. In contrast, achieving p-type conductivity in ZnO is quite challenging due to its propensity to create compensating donor defects and the relatively large energy necessary to create unfilled states in the deep valence band [9].

Candidate p-type dopants include the group V anions on the oxygen site or group I or IB elements on the Zn site. Previous studies [11,12] indicate that group I elements, namely Li, Na or K, do not easily incorporate on the Zn site, but rather occupy interstitial sites. Most research efforts have focused on the group V dopants, including N [31,134],
As [33,34], P [35-37] and Sb [38]. N is the most favored dopant candidate for p-type doping in ZnO based on similar bond length, low ionization energy and lack of antisite $N_{Zn}$ defects [39]. Experimentally, the solubility of N in ZnO appears to be low. Furthermore, the tendency to form N-N complexes that are not acceptor defects further reduces the effectiveness of this dopant. In practice, only a small fraction of the N incorporated into ZnO is observed to be electrically active. The remaining inactive N may act as scattering centers, possibly resulting in low carrier mobility [45]. Moreover, O-poor growth conditions are required to incorporate group V dopants onto the O sites. This growth condition promotes the formation of “hole-killer” defects yielding compensation [39, 45-47]. Calculations for As, P, or Sb substitution on the O lattice site predict high energies of formation and high acceptor-ionization energies. Both computational and experimental evidence suggest that the acceptor states observed for As, P, or Sb doped ZnO may be the result of complexes involving Zn site vacancies and group V dopants on the Zn site [135,136]. While several groups have been successful in achieving p-type conductivity via group V doping [31, 33-39,134,137], low carrier mobilities and carrier concentration remain important issues.

In comparison to the group V elements, studies on group IB dopants, namely Cu or Ag, in ZnO have been rather limited [66-68]. Early reports argued that Ag substitution in ZnO forms a deep acceptor state 0.23 eV below the bottom of the conduction band [69]. However, recent studies suggest this may not to be the case. One study reported an acceptor state binding energy for the Ag $3d^{10}$ states of only 200 meV [70]. Another study of the behavior of Ag in bulk ZnO suggests that Ag acts as an amphoteric dopant, yielding an acceptor state for substitution on the Zn site, and a donor state for interstitial
defects [71]. First-principles calculations have examined the dopant energy levels and
defect formation energies for group IB elements in ZnO [66]. The calculations estimate
the acceptor state ionization energies for substitutional Ag, Cu, and Au to be 0.4, 0.7,
0.5 eV, respectively. Although these represent relatively high ionization energies, the
formation energies for these substitutional defects (Cu_{Zn}, Ag_{Zn}, and Au_{Zn}) are predicted
to be low; energies for interstitial defects are predicted to be high. These calculations
suggest that solubility and self-compensation may be less of an issue for group IB
elements as compared to the group V dopants.

Within the group IB elements, Ag has the lowest predicted transition energy (0.4
eV) [66], reflecting a weaker p-d orbital repulsion as compared to Cu or Au. This weak
repulsion is rooted in the large size and low atomic d-orbital energy of Ag. Interestingly,
the O-rich conditions that have been suggested for preventing oxygen vacancy (V_O)
and/or Zn interstitial (Zn_i) defects are consistent with the required conditions for
substituting Ag onto the Zn site. A few groups have experimentally examined the
properties of Ag-doped ZnO. H. S. Kang et al. have reported the formation of p-type
ZnO via Ag doping in thin films grown by pulsed laser deposition [71]. The formation of
p-type material was limited to deposition temperatures of 200-250ºC. Studies on Ag-
implanted ZnO suggest that Ag substitution on the Zn site becomes unstable at
temperatures greater than 600ºC [72]. This is consistent with the estimated 0.08 mol%
bulk solid solubility of Ag in ZnO [73]. In this chapter, the synthesis and properties of Ag-
doped ZnO films grown by pulsed laser deposition is examined, focusing on the
formation of p-type material, as well as delineating the stability of the transport
properties.
4.2 Experimental Procedures

The ZnO:Ag ablation targets were fabricated using ultra high purity ZnO and Ag$_2$O powders. The concentration of Ag in the ZnO targets was 0.6 at%, and 0.3 at%. As mentioned before, the Ag content was somewhat arbitrary, made based on some rough assumptions regarding activation energy of the acceptor and desired hole concentration. The ZnO:Ag films were grown on c-plane (0001) sapphire substrate at temperatures ranging from 300 °C to 600 °C in oxygen partial pressure ranging from 1.0 to 75 mTorr. In specific occasions, undoped ZnO buffer layers were grown in 1.0 mTorr of oxygen at 400 °C or 800 °C. A KrF excimer laser was used as the ablation source at a frequency of 1.0 Hz with an energy density of 1.5 J/cm$^2$. The film thickness varied from 300 nm to 1.1μm for the ZnO:Ag thin films while the ZnO buffer (when employed) thickness was kept fixed at 50 nm. High-resolution x-ray diffraction (Phillips, XRD3720) was used to characterize the crystal quality of the films. Atomic force microscopy (AFM Dimension 3100) was used to observe the surface morphology. The resistivity, Hall mobility and carrier concentration were measured using a four-point van der Pauw method with a commercial LakeShore Hall measuring system. Measurements were taken in the dark, room light and various UV light wavelengths, in order to analyze the behavior of photocarriers in the doped films. The room temperature optical properties were analyzed using photoluminescence. For this, a He-Cd laser operating at 325 nm was used for excitation.

4.3 Results and Discussions

4.3.1 Role of Ag Doping in ZnO Crystal Quality and Surface Morphology

The crystalline structure and orientation of the deposited ZnO:Ag films was examined using x-ray diffraction. Figure 4-1a shows a log plot of the diffraction data for
films grown in 25 mTorr oxygen for the deposition temperatures ranging from 300-600ºC. The results showed that the films are c-axis oriented and ZnO is the primary phase. The diffraction does show the emergence of a secondary impurity phase for growth at 400 ºC and 500 ºC. The small, broad peak could be associated with either Ag₂O or Ag metal. In order to delineate the bonding state of the Ag, X-ray photoelectron spectroscopy (XPS) was performed on these films. The results show that both Ag and Ag₂O bonding energies are present in the films with the impurity peak in the diffraction pattern. Above 300 ºC Ag₂O is not stable and losses oxygen. Under these conditions, the formation of Ag metal is expected for any Ag segregation, however, Ag quantities are very small and no continuous secondary phase is observed. Figure 4-1b shows the diffraction data for films grown at 300 ºC for oxygen pressures ranging from 1-75 mTorr. For growth at this low temperature, the impurity peak is not observed in the diffraction data for the oxygen pressures considered. Also note that the ZnO (110) orientation was not observed for growth at 300 ºC. No significant shift in d-spacing from that for undoped ZnO was detected due to doping (Figure 4-2).

The surface morphology of the films was examined using atomic force microscopy (AFM). Figure 4-3 shows AFM images for films grown at 300ºC, 400ºC and 500ºC in an oxygen partial pressure of 25 mTorr. The grain size increased with increasing temperature and Ag inclusion. Note that an enhancement in grain size via the inclusion of Ag in the deposition flux has been reported for various oxide thin film materials [138,139]. In these experiments, it was speculated that the formation of Ag₂O in oxide growth provides a source of atomic oxygen through the continuous formation and dissociation of Ag₂O. The grain size measured for undoped ZnO was approximately
150 nm. For films grown under the same condition but doped with Ag, the grain size increased to 275 nm. The grain size of films grown at 400°C and 500°C was 390 and 560 nm, respectively. The AFM results show that as growth temperature is increased, roughness also increased. At 300 °C the average roughness was 5.36 nm while at 400 °C and 500 °C the roughness increased to 17.62 nm and 28.24 nm respectively. As for thicker films, the roughness increased drastically. As mentioned above, the highest roughness reported for films with thickness less than 500 nm was 28.24 nm, while films with thickness above 1.0 μm showed roughness as high as 100 nm. Such high roughness makes it difficult to obtain reliable transport and optical properties. Growing on mismatched substrates like sapphire introduces strain and a high density of interface defects that may result in inhomogeneous carrier concentration measurements that may yield the wrong carrier type [65]. It is worth noting that the surface of the thick SZO films showed dark spots which may block any light coming out of the films during optical characterization. Therefore, in an attempt to obtain smooth, clear and low defect films, 50 nm thick ZnO buffer layers were grown at 400 °C and 800 °C in 1.0 mTorr of oxygen prior to the growth of the 1.0 μm thick SZO film. The results showed that high temperature buffers (HTB), grown at 800 °C, improve the roughness of the thicker SZO films to 25nm and when the HTB is grown on ZnO substrates the SZO films roughness drops below 10 nm (Figure 4-4). In addition, SZO films grown with a high temperature buffer layer resulted in clear surfaces as shown in Figure 4-5.

4.3.2 P-Type Conductivity, Transport and Optical Stability of Ag-Doped ZnO Films

The transport properties of the films were determined using room temperature Hall measurements. As explained in chapter 3, in order to reliably delineate the carrier
type and density for these highly compensated samples, the Hall measurements were performed at various magnetic field values and over a large magnetic field range. Figure 4-6 shows a plot of $V_{\text{Hall}}d/I$ as a function of applied magnetic field, where $V_{\text{Hall}}$ is the Hall voltage, $d$ is the film thickness, and $I$ is the measurement current. It shows a plot of $V\cdot d\cdot I^{-1}$ as a function of magnetic field for two samples, a Ag-doped ZnO film grown at 600 °C that is n-type (as determined by the full Van der Pauw four-point calculation), and another film grown at 300 °C that is p-type. For the sample grown at 600 °C, the slope is clearly negative, indicating n-type. In Figure 4-6b, there is an obvious positive slope to the data as field is increased, indicating p-type behavior. From the slope of the curve, the extracted hole carrier density is $5.2\times10^{16}$ cm$^{-3}$.

Figure 4-7 shows the results for resistivity and carrier concentration of 0.6 at% SZO films for some of the growth conditions considered. For most deposition conditions, the films were n-type (Table 4-1). For growth temperatures in the range of 300-500°C, results showed an initial drop in film resistivity, followed by a rise as growth pressure was increased. P-type ZnO was realized for films grown at 400 - 500 °C in oxygen pressure of 10 and 25 mTorr. For p-type material, these conditions were optimal. For these films, the hole carrier concentration was in the mid-$10^{19}$ cm$^{-3}$. The mobility for films grown at 400 °C and 500 °C was 10.7 and 2.9 cm$^2$/Vs, respectively. Note that for growth at 300 °C, P(O$_2$)=75 mTorr, and 400 °C and 500 °C in 10mTorr of oxygen, low carrier concentration p-type ZnO:Ag was also realized. At a growth temperature of 600 °C, the carrier concentration and resistivity were independent of growth pressure. Presumably, the Ag was driven out of the Zn site yielding only n-type films. All films grown with Ag content other than 0.6 at% were n-type.
ZnO:Ag films grown at 300 °C, P(O_2) = 75 mTorr were stored in the dark and Hall measurements were performed to study the stability of the transport properties over time. Before storing in the dark, the samples were exposed to indoor room light for approximately 24 hours. Figure 4-8 shows resistivity vs. time for a film grown at 300 °C in 75 mTorr of O_2. Note that this was a different film from that considered in figure 4-6b, and exhibited a higher resistivity. Results demonstrate a large increase in resistivity from 694 to 3704 Ω-cm in the first week of dark storage. This spike in resistivity is mainly due to the relaxation of persistent photocarriers created by light exposure. After a week in the dark, the resistivity of the film gradually decreases. When considering the long-term stability of the Ag-doped ZnO films, one may need to consider the possible effects of oxygen absorption, hydroxide formation, or diffused hydrogen, the latter being important since the hydrogen diffusion rate is quite high. This may be the cause of the subsequent decrease in resistivity and change in carrier type. The change in carrier type was observed just after 120 days of storage. Another set of films grown in the same conditions were exposed to three different UV-light wavelengths (365, 304, and 254 nm) after being stored in the dark for some time. A persistent photoconductivity was observed as shown in Figure 4-9a. The drop in resistivity was independent of the wavelength used. The relaxation time for this set of films was about 24 hours. Figure 4-9b shows the conductivity curve as a function of time when films are placed in the dark after UV light exposure. An exponential decay curve can be fitted and the relaxation time constant, τ, was extracted to be 227.9 min.

Room temperature photoluminescence measurements were performed on the Ag-doped ZnO films. The PL spectra are shown in Figure 4-10. The Ag-doped ZnO
films showed well-defined band edge emission around 377 nm. This emission line is due to free exciton recombination around 3.27 eV, which is very close to the bandgap (3.25 eV) found by room temperature absorption measurements shown in Figure 4-11. The photoluminescence intensity was highest for films grown at 400 - 500ºC. This enhancement may be due to a reduction in surface states, which are deleterious to UV emission. Other studies on the effect a monovalent dopant on the photoluminescence of ZnO showed that Ag enhances the efficiency of exciton recombination, so as to have better optical properties [68]. Note that there is little visible emission often seen in ZnO films [140] due to recombination involving mid-gap states suggesting lower concentration of compensating defects in the films.

4.4 Summary

The synthesis and properties of Ag-doped ZnO thin films were examined. Epitaxial ZnO films doped with 0.6 at% Ag content grown at moderately low temperatures (300 ºC to 500 ºC) by pulsed laser deposition yielded p-type material as determined by room temperature Hall measurements. Hole concentrations on the order mid-10\(^{15}\) to mid-10\(^{19}\) cm\(^{-3}\) range were realized. Growth at higher temperatures yielded n-type material, suggesting that the Ag was driven out of the substitutional site above 500 ºC and that Ag substitution yielding an acceptor state is metastable. Photoluminescence measurements showed strong near-band edge emission with little mid-gap emission as the result of Ag substitution for Zn (Ag\(_{\text{Zn}}\)) and reduction of surface states deleterious to UV photoluminescence emission. The stability of the Ag-doped films was examined as well. Presumably hydrogen incorporation caused the films to turn n-type after about 120 days. Persistent photoconductivity was also observed. High temperature ZnO buffer layers drastically improved the surface morphology of films thicker than 1.0 µm.
roughness below 10 nm were observed. Finally, in developing electroluminescent junctions, the realization of robust UV photoluminescence in p-type ZnO may prove advantageous. A detailed PL study and results for the rectifying junctions utilizing Ag-doped ZnO films are reported in the following chapters.
<table>
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<td></td>
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</tbody>
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Figure 4-1. Powder XRD pattern for films grown in (a) 25 mTorr for deposition temperature range of 300-600 °C, and (b) films grown at 300 °C in oxygen pressures ranging from 1-75 mTorr.
Figure 4-2. Effect of Ag doping on ZnO d-spacing for films grown at 500 °C

Figure 4-3. AFM images for films grown at (a)(b) 300°C, (c) 400°C, and (d) 500°C
Figure 4-4. SZO film average roughness as a function of Ag content grown on different substrates and buffer layers.

Figure 4-5. Optical microscope images of the surface of ZnO grown (a) without buffer layer and (b) with HTB layer.
Figure 4-6. Plot of $V \cdot d/I$ as a function of magnetic field for (a) an n-type and (b) a p-type Ag-doped ZnO film.
Figure 4-7. Resistivity (a) and carrier concentration (b) as a function of growth conditions.
Figure 4-8. Resistivity as a function of time for films grown at 300 °C, P(O₂) = 75 mTorr
Figure 4-9. Effects of (a) UV light exposure and dark storage, showing (b) exponential decay of conductivity over time in dark storage for films grown at 300°C, P(O₂) = 75 mTorr.

Conductivity (Ω·cm⁻¹) vs. time (min)

σ = C₀e^(-t/τ)

C₀ = 0.02284 Ω·cm⁻¹
τ = 227.85 min
Figure 4-10. Room temperature photoluminescence for Ag-doped ZnO films grown at various temperatures in 25 mTorr of oxygen showing (a) large wavelength and (b) narrow wavelength plots.
Figure 4-11. Room temperature absorption spectra for Ag-doped ZnO
Light emitting diodes are expected to develop as a major market; therefore, it is important to investigate the optical properties of different ZnO films. Not only does it help to analyze the structure and other properties of ZnO, but also it contributes to the optimization of the growth process of ZnO. In order to make high-performance optoelectronic devices on ZnO, it is necessary to investigate the transitions processes in ZnO.

The main optical transitions seen in ZnO originate from free excitons, bound excitons, two-electron satellites (TES) and donor-acceptor pairs. The related free-exciton transitions involving an electron from the conduction band and a hole from ZnO three valance bands are named as A (corresponding to the heavy hole), B (corresponding to the light hole), and C (corresponding to crystal field split band). These transitions dominate the near bandgap intrinsic absorption and emission spectra and occur at energies between 3.37 and 3.45 eV. Bound exciton emissions originate from discrete electronic energy levels caused by dopants or defects. Normally, neutral shallow donor-bound exciton transitions dominate the low temperature PL spectrum due to the presence of donor sources (unintentional impurities or other shallow-level defects) and they occur at energies between 3.34 and 3.37 eV. Acceptor-bound exciton transitions are sometimes seen in ZnO samples that contain a substantial amount of acceptors and can be seen at energies between 3.30 and 3.35 eV. TES transitions occur at this same range in high quality ZnO samples. This transition process is generated by the radiative recombination of an exciton bound to a neutral donor, leaving
the donor in the excited state (2s or 2p state). Emissions originated from donor-acceptor recombination and respective phonon replicas are expected at energies between 3.05 and 3.26 eV.

There are a lot of experimental techniques for the study of the optical transitions processes in ZnO. In this chapter the defects in ZnO are analyzed in detail using both room temperature and low temperature (15 K) photoluminescence spectroscopy. Furthermore, the effect of co-doping, grain growth and different buffer layers on the optical properties of ZnO is discussed.

5.2 Experimental

In this study, several films with different dopants were grown via pulsed laser deposition. Ag, P, and Ga were used individually to dope ZnO, while co-doped ZnO was realized using Ag and P. The Ag content in the ZnO ablation target was 0.6 at%. The other ablation targets were fabricated using ZnO doped with 0.5 at% P, and ZnO doped with 0.22 at% Ga content. Co-doped ZnO ablation target was fabricated using 0.5 at% P and 0.6 at% Ag. The films were grown on single crystal c-oriented sapphire and GaN substrates. Prior to growth, the substrates were cleaned in an ultrasonic bath using trichloroethylene, acetone, and methanol. The substrates were attached to the heater plate using silver paint. The substrate to target distance was 3.5 cm. Some of the Ag-doped ZnO samples were grown on a high temperature ZnO buffer layers. The growth temperature and P(O₂) was 800 °C and 1 mTorr respectively and were 50 nm thick. ZnO lattice-matched MgCaO buffers grown on GaN substrate via molecular beam epitaxy (MBE) were also employed in this study. Note that buffer layers fabricated using MBE were grown by another research group, thus, this section discuss only the effects on photoluminescence properties. Table 5-1 lists the growth condition, doping content, and
heat treatment used for all samples analyzed. The resistivity, Hall mobility and carrier concentration were measured using a four-point van der Pauw method. Contacts for the Hall measurements were soldered indium. Photoluminescence was measured using a He-Cd continuous-wave laser operating at 325 nm. A CTI Cryogenic vacuum pump was used to lower the temperature of the samples during low temperature and temperature dependent PL measurements.

5.3 Results and Discussions

5.3.1 PL Enhancement via Ag Inclusion

The room temperature PL spectra of undoped ZnO (s1) and Ag-doped ZnO (s2) are shown in Figure 5-1. The undoped sample shows two characteristic emission bands. The near band edge emission centered at 377 nm which originates from free exciton recombination [141] and a dominant broad deep level emission centered at 505 nm, which originates from structural defects and impurities [142]. The Ag-doped sample shows the opposite behavior, an enhanced UV emission (383 nm) and a suppressed deep level emission. Other studies on the effect a monovalent dopant on the photoluminescence of ZnO showed that Ag enhances the efficiency of exciton recombination, so as to have better optical properties [68]. It has been suggested that if Ag occupies a Zn site (Ag\text{Zn}), photocarriers may escape more easily from Ag ions resulting in more excitons and higher excitonic recombination. As discussed in the previous chapter, Ag inclusion also causes grain growth which results in smaller non-radiative relaxation rates over the surface states [143] and thus better exciton diffusion through the crystal and higher UV PL intensities. Figure 5-2 shows the UV emission PL intensity increasing as a function of increasing grain size. The intensity increased from 0.75 abs. units to 8.4 abs. units as grain size increased from 168 nm to 330 nm.
respectively. Further grain growth to 560 nm resulted in higher PL intensity (11.7 abs. units). The suppression of the broad deep band suggests that Ag does not occupy an interstitial site or an antisite [144].

**5.3.2 Low Temperature and Temperature Dependent PL**

Hwang *et. al.* [145], resolved both donor and acceptor bound exciton transitions in high quality undoped ZnO. The PL spectra measured at 10 K is shown in Figure 5-3. The undoped sample shows two main peaks. A strong PL emission centered at 3.363 eV which originates from localized exciton recombination bound to a donor state (D^0X) [31, 144-148]. The next PL peak is slightly weaker and it is centered at 3.352 eV and has been previously identified as the acceptor-bound exciton transition (A^0X) [149]. Meyer *et al.* [146] showed that PL emission originating from donor-acceptor pairs (DAP) and DAP LO phonon replicas can be found centered at 3.24 eV and 3.17 eV, respectively. The nature of the acceptor state is unclear, however emission from free exciton to neutral acceptor transitions (e, A^0) are expected around 3.31 eV [144,145,150] but are rarely seen in undoped samples. Similarly, the Ag-doped sample shows a series of main peaks followed by small shoulders shown in Figure 5-4. The first peak centered at 3.353 eV corresponds to A^0X emissions, preceded to its right by a small shoulder around 3.36 eV corresponding to D^0X. A strong peak centered at 3.31 eV dominates the spectrum. As mentioned above this emission originates from free electrons to neutral acceptor state transitions, in this case, believed to be Ag related. It should be noted that the PL intensity from D^0X (3.36 eV) is relatively small compared to the A^0X and (e,A^0) peaks suggesting that the Fermi level should be near the acceptor level. This is consistent with the p-type conductivity of the sample measured by Hall (see Figure 5-5). These results are also consistent with those found in P-doped ZnO by
Li et al [150]. The following shoulders centered at 3.25 eV and 3.17 eV correspond to DAP and DAP-LO emissions, respectively.

Temperature dependent PL was employed to further study the nature of the main peaks centered at 3.35 eV and 3.31 eV. Figure 5-6 is a plot of peak position as a function of temperature. Increasing the temperature causes the (e,A⁰) peak position to blue-shift at low temperatures from 15 K to 110 K, followed by a red-shift at higher temperatures. This is a typical behavior seen in PL peaks assigned to radiative recombination of free-neutral acceptor [144,150]. The acceptor energy of the Ag dopant was estimated from the free-to-neutral-acceptor transition at 3.311 eV. The transition energy is given by

\[ E_{eA} = E_g - E_A + \frac{K_B T}{2} \]  

(7)

where \( E_g \) and \( E_A \) are the band gap and acceptor energies, respectively. Since the thermal energy can be neglected at 15 K, the acceptor energy can be roughly estimated \( E_A = E_g(3.437) - E_{eA}(3.313) \) to obtain 124 meV.

Finally, in order to delineate the excitonic nature of the peak centered at 3.352, Ag-doped ZnO films with different grain sizes, s2 and s3, were compared at low temperatures. The low temperature PL spectra showed that both peaks assigned A⁰X and (e,A⁰) drastically increased their intensities with grain size. As shown in Figure 5-7, the peak A⁰X intensity increased from 81 abs. units (s2) to 136 abs. units (s3), a 68.7% increase in emission intensity with increasing grain size. The (e,A⁰) peak intensity increased 12.7 % from 213 abs. units (s2) to 240 abs. units (s3), while other non excitonic peaks and shoulders remained relatively unchanged. The grain size of s2 and s3 is 333 nm and 560 nm respectively. Exciton diffusion through the crystal is expected
to improve with grain growth and lowering of surface states, hence the drastic increase in intensity from the A^0X peak (3.35 eV). In the case of free electrons, fewer surface states and lower relaxation rates are expected to aid in their recombination process. Such PL intensities and shallow acceptor energy suggest that Ag can yield a robust acceptor level.

**5.3.3 Buffer Layer and Dopant Effect on the Optical Properties of ZnO**

In the previous sections, it was discussed how Ag inclusion improves the optical properties of ZnO as well as yielding an acceptor state clearly identifiable by PL measurements. In order to further improve the PL properties of ZnO, a high temperature buffer (HTB) and a lattice-matched MgCaO buffer were employed individually prior to the growth of Ag-doped films. Figure 5-8 compares the room temperature PL results.

The near band edge emission is centered at 378 nm for all samples. As mentioned above the enhancement in the UV PL is readily seen when ZnO is doped with Ag. UV PL intensity increased further with the use of the HTB, while the maximum intensity is observed when the lattice-match MgCaO is employed. The HTB reduces surface states by improving the surface roughness and clearing the surface from dark spots as shown in chapter 4, enhances UV PL emission of the films. Improvement in roughness and less structural defects was also observed when the lattice-matched MgCaO buffer was employed. In addition, the MgCaO buffer may induce band bending in ZnO at the interface changing the electronic states of the defects responsible for visible emission and thus enhancing the UV emission [148,149] further.

Figure 5-9 shows the room temperature PL spectra of ZnO doped with different elements. The Ag-doped ZnO sample has a stronger UV emission than any other
sample including Ga-doped ZnO, which is currently used in most ZnO-based heterojunctions. Codoping ZnO with Ag and P deteriorated the optical properties.

5.4 Summary

Silver-doped ZnO films were grown via PLD and their optical properties were discussed. Results showed that Ag inclusion lead to grain growth and smaller non-radiative relaxation rates over surface states, which lead to UV emission enhancement. Room temperature PL measurements also showed a suppression of ZnO visible luminescence suggesting that Ag does not occupy interstitial sites or an antisite.

Low temperature and temperature dependent PL spectroscopy revealed strong and dominant emissions originating from free electron recombination to Ag-related acceptor states around 3.31 eV. The AºX emission at 3.352 eV was also observed at low temperatures. Enhancement of the PL intensity with increasing grain size, and the peak position blue-shifts (low temperatures) followed by red-shifts (high temperatures) with increasing temperature, confirmed the nature of the emission. Donor-acceptor pair emission and corresponding phonon replicas were also observed. The acceptor energy was estimated to be 124 meV. The very weak deep level emission (not shown), again in the low temperature PL spectra indicates that in the p-type ZnO:Ag native donor and acceptor defects are suppressed suggesting the observed acceptor related PL emissions and hole concentration are from the Ag in ZnO instead of native defects.

High temperature ZnO buffers and lattice match MgCaO buffers helped improve the UV emission of the Ag doped films. A combination of band bending at the MgCaO-ZnO interface and reduction of surface states may be responsible for such enhancement. No visible luminescence was observed. Finally, the room temperature PL
spectrum of Ag-doped ZnO was compared to that of undoped, P-doped, Ga-doped, and Ag-Ga- codoped ZnO. The Ag-doped ZnO films showed better optical properties.
<table>
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<th>Growth Temperature</th>
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Figure 5-1. Room temperature PL spectra of undoped ZnO and Ag doped ZnO

Figure 5-2. Band Edge Intensity as a function of grain size
Figure 5-3. PL spectra of undoped ZnO measured at 10 K Reprinted with permission from Figure 1 of D. K. Hwang, H.S. Kim, J.H. Lim, Appl. Phys.Lett. 86, (2005) 151917.

Figure 5-4. PL spectra of Ag-doped ZnO (s2) measured at 15 K
Figure 5-5. Plot of $V \cdot d \cdot I^{-1}$ as a function of magnetic field for p-type Ag-doped ZnO s2

Figure 5-6. Acceptor related peak positions as a function of increasing temperature
Figure 5-7. PL intensity-grain size relationship for localized bound exciton in Ag-doped ZnO

Figure 5-8. Room temperature UV PL emission of Ag doped ZnO grown on different buffer layers
Figure 5-9. Room temperature PL spectra for ZnO doped with different elements.
CHAPTER 6  
ZINC OXIDE DEVICES

6.1 Introduction

An important issue in developing ZnO-based electronics is the formation of p-type material and rectifying junctions [128, 129]. Studies have indicated that Ag can act as an amphoteric dopant, yielding an acceptor state for substitution on the Zn site, and a donor state for interstitial defects [70]. In the previous chapters, it was shown that Ag is more likely to occupy a substitutional site yielding acceptor state for selected growth conditions. Moreover, first-principles calculations have been used to estimate the dopant energy levels and defect formation energies for Ag in ZnO [66]. The calculations estimate the acceptor state ionization energies for substitutional Ag to be 0.4 eV. Although this predicted value for ionization energy is relatively high, the formation energy for this substitutional defect (Ag\textsubscript{Zn}) is predicted to be low; energies for interstitial defects are predicted to be high. H. S. Kang et al. recently reported the formation of p-type ZnO via Ag doping in thin films grown by pulsed laser deposition [67]. This study has also examined the growth conditions and stability of p-type Ag-doped ZnO films. Results showed p-type conductivity with carrier concentrations as high as 5x10\textsuperscript{19} cm\textsuperscript{-3}, as well as, excellent UV photoluminescence emission. In this chapter, the fabrication and properties of rectifying Ag-doped ZnO/Ga-doped ZnO thin film junctions is reported.

6.2 Experimental

As mentioned above, film growth experiments over a wide range of deposition conditions revealed a deposition parameter space where p-type SZO thin films could be realized (see Table 4-1). The p-type conductivity in the Ag-doped ZnO layers was confirmed using Hall measurements taken at various magnetic fields. For the films and
devices considered in this chapter, including junctions, the p-type SZO films and layers were grown at 500 °C in an oxygen pressures of 10 and 25 mTorr.

6.2.1 Silver-Doped ZnO / Gallium-Doped ZnO Thin Film Homojunction

The Ag-doped ZnO films were grown via pulsed laser deposition. A 254 nm KrF excimer laser was used as the ablation source. The laser was operated at a repetition rate of 1 Hz and an average energy density of 1 J/cm$^2$. Ablation targets were fabricated using ultra high purity ZnO and Ag$_2$O powders. The targets were sintered at 1000 °C in air. The concentration of Ag in the ZnO target was 0.6 at%. Single crystal c-plane sapphire substrates were employed for this study. Prior to growth, the substrates were cleaned in an ultrasonic bath using trichloroethylene, acetone, and methanol. The substrates were attached to the heater platen using silver paint. The substrate to target distance was 3.5 cm. Ag-doped ZnO layer thickness varied from 250 nm to 450 nm. Ga-doped ZnO laser ablation targets were fabricated with high purity (99.9995 %) ZnO mixed with gallium oxide (99.998 %) as the doping agent. The gallium doping level in the target was 1 at. %. Ga-doped ZnO, which served as the n-type layer, was grown on c-plane sapphire at 700 °C in an oxygen pressure of 1 mTorr. Otherwise, the ablation conditions are as described above for the Ag-doped ZnO film. The thickness for the n-type Ga-doped ZnO layer was about 350 nm. The resistivity, Hall mobility and carrier concentration were measured using a four-point van der Pauw method. Contacts for the Hall measurements were soldered indium. Photoluminescence was measured using a He-Cd continuous-wave laser operating at 325 nm. Finally, the I-V characteristics of Ag-doped ZnO/Ga-doped ZnO junctions were analyzed.


6.2.2 Silver-Doped ZnO Thin Film Transistor (TFT)

A bottom gate thin film transistor (TFT) using Ag doped ZnO as the active (p-type) layer was fabricated. The film was grown by pulsed laser deposition. A 254 nm KrF excimer laser was used as the ablation source. The laser was operated at a repetition rate of 1 Hz and an average energy density of 1 J/cm². Ablation targets were fabricated using ultra high purity ZnO and Ag₂O powders. The targets were sintered at 1000 °C in air. The concentration of Ag in the ZnO target was 0.6 at%. A heavily doped p⁺ Si wafer was used as substrate. The thermal oxide (SiO₂, dry oxygen source) was 100 nm thick. The source and drain electrodes were patterned by shadow mask. Ni and Au metal contacts were used and the thickness was 20 nm and 80 nm, respectively. The width and length of the electrodes was 750 nm and 50 nm, respectively. The gate was open by photolithography and buffer oxide etch (BOE) etching (1:6, 4 minute etch) and the metal used was Indium. The as grown Ag-doped ZnO film was grown without etching to form the specific pattern of the channel. Figure 6-4 shows the schematic of the TFT.

6.3 Results and Discussion

6.3.1 Rectifying Thin Film Junction

Table 6-1 shows the transport properties of Ag-doped and Ga-doped ZnO films grown under corresponding conditions. Figure 6-1 shows a plot of \( V_{Hall}d/I \) as a function of applied magnetic field and room temperature photoluminescence for a Ag-doped ZnO grown at 500 °C in an oxygen pressure of 25 mTorr. The pn junction fabrication started with device isolation and followed with p-mesa definition using dilute phosphoric acid solution. Electron beam deposited Ni (20nm)/Au (80nm) and Ti (20nm)/Au(80nm) were used as the p- and n-Ohmic metallization. Figure 6-2 shows a schematic of the devices fabricated as well as the test for Ni-Au contacts. The size of the devices was 180μm in
diameter for the active area. A rectifying behavior is observed in the I-V curve as seen in Figure 6-3, consistent with the Ag doped ZnO layer being p-type and forming a pn junction with the Ga-doped ZnO layer. The forward bias turn-on voltage for the junction shown was 3.0 V. Reverse bias breakdown occurred at approximately 5.5 V. This rectifying behavior is similar to that seen for ZnO junctions incorporating group V dopants [151,152]. Note that, without the metallization of contacts, the device was optically transparent in the visible range. Also, note that the deposition of the layered structure in reverse order (Ag-doped ZnO on bottom, Ga-doped ZnO on top) did not result in rectifying I-V characteristics as shown in Figure 6-4. The reason for this is unclear but may relate to the differing growth temperatures used for the two layers.

The rectifying junction was then examined for light emission intensity. The current-voltage (I-V) characteristics were measured at 300 K using a probe station and Agilent 4145B parameter analyzer. The emission output power from the structures was measured using a Si photodiode. The results for multiple measurements on a typical rectifying junction are shown in Figure 6-5. Note that the non-zero light emission with no excitation current is an artifact of the null offset for Si photodiode. The highest emission output power measured was $5.2 \times 10^{-8}$ mW. The excitation current used did not exceed 20 mA. At 10mA, the applied voltage was approximately 2.0 V. Several devices were fabricated that displayed these characteristics. Note that, after each measurement, the light intensity decreased. The junction became ohmic after only a few measurements. Subsequent annealing of these junctions did not result in recovery of the light emission or rectifying I-V characteristics. Unfortunately, the relatively unstable nature of light emission under bias made it not possible to obtain a useful electroluminescence.
spectrum. The instability appears to be related to surface conduction and perhaps hydrogen incorporation as discussed elsewhere [153,154].

6.3.2 Silver Doped ZnO TFT

Figure 6-5 shows the measured output and transfer characteristics of Ag-doped ZnO TFT grown on Si. Note that the channel behavior is that of an n-type TFT operating in charge accumulation mode. The reason for the n-type behavior of Ag-doped ZnO is unclear. It is believed that growing ZnO on Si may have altered the conductivity of the film by changing its crystallinity from single to polycrystalline. The mobility of the channel was 3.5 cm²/Vs and the I_{on}/I_{off} ratio was 10⁵. The determined subthreshold slope is 4.4 V/decade. This value suggests that the crystallinity of the channel is very poor.

Fabrication of a TFT structure on sapphire (Al₂O₃) is expected to yield better film crystallinity and not to affect the conductivity of the channel, possibly resulting in a p-channel TFT.

6.4 Summary

In previous chapters, results showed p-type conductivity in Ag-doped ZnO with carrier concentrations as high as 5x10¹⁹ cm⁻³, as well as, excellent UV photoluminescence emission. In this chapter, the fabrication and properties of rectifying Ag-doped ZnO/Ga-doped ZnO thin film junctions were reported. A rectifying behavior was observed in the I-V characteristic, consistent with Ag-doped ZnO being p-type and forming a p-n junction. The turn on voltage of the device was 3.0 V under forward bias. The reverse bias breakdown voltage was approximately 5.5 V. Devices were optically transparent in the visible range. The highest light emission output power measured was 5.2x10⁻⁸ mW. At excitation currents of 10 mA, the applied voltage was approximately
2.0 V. After each measurement the light intensity decreased and the junction became Ohmic. The instability appears to be related to surface conduction and perhaps hydrogen incorporation. Finally, deposition of layers in reversed order (Ag-doped ZnO on bottom, Ga-doped ZnO on top) did not result in rectifying I-V characteristics. The reason for this is unclear but may relate to the differing growth temperatures used for the two layers.

Thin film transistor structures were also fabricated. Although no p-channel behavior was observed, the measured output and transfer characteristics revealed a mobility of 3.5 cm$^2$/Vs and a $I_{on}/I_{off}$ ratio of $10^5$. The subthreshold slope was determined to be 4.4 V/decade.
Table 6-1. Properties of n-type and p-type materials used in the junction device

<table>
<thead>
<tr>
<th>Transport Properties</th>
<th>Ga-doped ZnO n-type</th>
<th>Ag-doped ZnO p-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity ($\Omega\cdot$cm)</td>
<td>0.00127</td>
<td>0.00198</td>
</tr>
<tr>
<td>Mobility (cm$^2$/V-s)</td>
<td>27.10</td>
<td>2.87</td>
</tr>
<tr>
<td>Carrier Concentration (cm$^{-3}$)</td>
<td>5.0x10$^{19}$</td>
<td>5.9x10$^{19}$</td>
</tr>
</tbody>
</table>
Figure 6-1. Plot of (a) $V_{Hall}/I$ as a function of applied magnetic field and (b) room temperature photoluminescence for a Ag-doped ZnO was grown at 500 °C in an oxygen pressure of 25 mTorr.
Figure 6-2. The ZnO:Ag/ZnO:Ga/sapphire junction (a) schematic of structure and (b) TLM test for Ni-Au contacts
Figure 6-3. Homojunction I-V characteristics
Figure 6-4. The ZnO:Ga/ZnO:Ag/sapphire junction (a) schematic of structure and (b) junction I-V characteristic.
Figure 6-5. The emission output power from the ZnO:Ag/ZnO:Ga/sapphire junction as measured using a Si photodiode.

Figure 6-6. Schematic of ZnO:Ag thin film transistor
Figure 6-7. ZnO TFT grown on Si - output and transfer characteristics
CHAPTER 7
CONCLUSIONS

The research presented in this dissertation focused on Ag-doped ZnO thin film growth by pulsed laser deposition for the understanding of Ag behavior as a p-type dopant of ZnO and realization of light emitting diodes. Firstly, Ag-doped ZnO films were investigated to understand the effect of Ag doping on ZnO structural, transport, and optical properties and to obtain robust p-type ZnO films. P-type ZnO films were achieved by doping with Ag without the need of post annealing steps. Photoluminescence properties were examined and optimized. Lastly, ZnO LEDs were fabricated by using Ag-doped p-type ZnO layer. Light emission was observed.

7.1 P-type Silver-Doped ZnO Films

The synthesis and properties of Ag-doped ZnO thin films were examined. Epitaxial ZnO films doped with 0.6 at% Ag content grown at moderately low temperatures (300 °C to 500 °C) by pulsed laser deposition yielded p-type material as determined by room temperature Hall measurements. Hole concentrations on the order mid-$10^{15}$ to mid-$10^{19}$ cm$^{-3}$ range were realized. Growth at higher temperatures yielded n-type material, suggesting that the Ag was driven out of the substitutional site above 500 °C and that Ag substitution yielding an acceptor state is metastable. Photoluminescence measurements showed strong near-band edge emission with little mid-gap emission as the result of Ag substitution for Zn (Ag$_{Zn}$) and reduction of surface states deleterious to UV photoluminescence emission. The stability of the Ag-doped films was examined as well. Presumably hydrogen incorporation caused the films to turn n-type after about 120 days. Persistent photoconductivity was also observed. High temperature ZnO buffer
layers drastically improved the surface morphology of films thicker than 1.0 μm. Roughness below 10 nm were observed for films grown on ZnO substrates.

7.2 Silver Related Acceptor State and Optimized Ultraviolet in Silver-Doped ZnO Thin Films

Silver-doped ZnO films were grown via PLD and their optical properties were discussed. Results showed that Ag inclusion lead to grain growth and smaller non-radiative relaxation rates over surface states, which lead to UV emission enhancement. Room temperature PL measurements also showed a suppression of ZnO visible luminescence suggesting that Ag does not occupy interstitial sites or an antisite.

Low temperature and temperature dependent PL spectroscopy revealed strong and dominant emissions originating from free electron recombination to Ag-related acceptor states around 3.31eV. The A°X emission at 3.352 eV was also observed at low temperatures. Enhancement of the PL intensity with increasing grain size, and the peak position blue-shits (low temperatures) followed by red-shits (high temperatures) with increasing temperature, confirmed the nature of the emission. Donor-acceptor pair emission and corresponding phonon replicas were also observed. The acceptor energy was estimated to be 124 meV. The very weak deep level emission (not shown), again in the low temperature PL spectra indicates that in the p-type ZnO:Ag native donor and acceptor defects are suppressed suggesting the observed acceptor related PL emissions and hole concentration are from the Ag in ZnO instead of native defects.

High temperature ZnO buffers and lattice match MgCaO buffers helped improve the UV emission of the Ag doped films. A combination of band bending at the MgCaO-ZnO interface and reduction of surface states may be responsible for such enhancement. No visible luminescence was observed. Finally, the room temperature PL
The spectrum of Ag-doped ZnO was compared to that of undoped, P-doped, Ga-doped, and Ag-Ga-codoped ZnO. The Ag-doped ZnO films showed better optical properties.

### 7.3 Rectifying pn Junction and TFT Devices

Both p-type conductivity in Ag-doped ZnO with carrier concentrations as high as $5 \times 10^{19}$ cm$^{-3}$, as well as, excellent UV photoluminescence emission were achieved. The fabrication and properties of rectifying Ag-doped ZnO/Ga-doped ZnO thin film junctions were reported. A rectifying behavior was observed in the I-V characteristic, consistent with Ag-doped ZnO being p-type and forming a p-n junction. The turn on voltage of the device was 3.0 V under forward bias. The reverse bias breakdown voltage was approximately 5.5 V. Devices were optically transparent in the visible range. The highest light emission output power measured was $5.2 \times 10^{-8}$ mW. At excitation currents of 10 mA, the applied voltage was approximately 2.0 V. After each measurement the light intensity decreased and the junction became Ohmic. The instability appears to be related to surface conduction and perhaps hydrogen incorporation. Finally, deposition of layers in reversed order (Ag-doped ZnO on bottom, Ga-doped ZnO on top) did not result in rectifying I-V characteristics. The reason for this is unclear but may relate to the differing growth temperatures used for the two layers.

An n-type Ag-doped ZnO TFT operating in charge accumulation mode was fabricated. The reason for the n-type behavior of Ag-doped ZnO is unclear. It is believed that growing ZnO on Si may have altered the conductivity of the film by changing its crystallinity from single to polycrystalline. The mobility of the channel was 3.5 cm$^2$/Vs and the $I_{on}/I_{off}$ ratio was $10^5$. The determined subthreshold slope is 4.4 V/decade. This value suggests that the crystallinity of the channel is very poor. Growing the Ag-doped ZnO TFT structure on sapphire, to avoid crystallinity issues has been suggested. The
conductivity is expected to remain p-type however a top gate TFT structure would be required.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Fernando Lugo was born in 1983, in Barquisimeto, Venezuela. After graduating from high school in 2001, he attended Miami Dade College and earned an Associate of Arts degree in May 2003. He then began to pursue a Bachelor’s degree at The University of Florida in Material Science and Engineering. He received his Bachelor’s degree in the spring of 2006. He conducted his undergraduate research for bachelor’s degree on the growth of ZnO materials for optoelectronic applications under the supervision of Dr. David P. Norton.

In summer 2006, he enrolled in graduate school at the University of Florida in the Department of Materials Science and Engineering to pursue a Ph.D. under the advisement of Dr. David P. Norton. His main research involved growth and characterization of ZnO thin films for light emitting diodes. He is a SEAGEP fellow and is the co-author of more than 10 journal and conference papers. He was a member of the University of Florida Ultimate Frisbee club team from 2007 to 2010.