Chapter 4

Electrical characteristics of n-ZnO/p-Si heterojunction diodes grown by pulsed laser deposition
Heterojunction diodes of n-type ZnO/p-type silicon (100) were fabricated by pulsed laser deposition of ZnO films on p-Si substrates in oxygen ambient at different pressures. Turn-on voltage of the heterojunctions was found to depend on the ambient oxygen pressure during the growth of the ZnO film. The current density-voltage characteristics and the variation of the series resistance of the n-ZnO/p-Si heterojunctions were found to be in line with the Anderson model and Burstein-Moss (BM) shift.
4.1. Introduction

Currently there is significant interest in ZnO as a candidate for various futuristic optoelectronic devices. ZnO is a rugged semiconductor with direct wide band-gap and it exhibits significant n-type conductivity even without any intentional doping. This n-type conductivity can be further enhanced by doping it with Al or Ga [1-3]. This property and the transparency in the visible spectral region have prompted extensive investigations of ZnO films as transparent electrodes in flat-panel displays [4], p-n heterojunction diode [5-7], thin film transistors [8], multiple quantum well structures [9] and solar cells [10]. We have fabricated ZnO based all transparent conducting p-n heterojunction diodes with p-type AgCoO$_2$ [11,12]. Albeit ZnO films can be grown by a variety of methods, including radio-frequency (rf) and direct-current (dc) sputtering [3,13,14], chemical vapor deposition [15], spray pyrolysis [16], electron cyclotron resonance-assisted molecular beam epitaxy [17], we used pulsed laser deposition (PLD) [1,18,19] to deposit high quality ZnO films because of its effectiveness and amenability to different growth conditions [20]. For the present study we fabricated heterojunctions of n-type ZnO on p-type Si, which has many advantages such as low cost, large wafer size and possibility of integrating oxide semiconductors with already highly matured silicon technology.

The growth of ZnO on Si substrates has been studied extensively including the epitaxial growth of ZnO on Si (100) substrates [21], ZnO/p-Si diodes [22-24], ZnO:N/p-Si heterostructures [25] etc. Studies on the electrical transport properties of ZnO/p-Si heterojunctions with different dopands in p-Si [26] and ZnO [27] have also been reported recently. However, due to the complex nature of the carrier transport across the interfaces of n-ZnO /p-Si
heterojunction, transport properties of these heterostructures are not yet well understood and even debatable. We have furthered these studies on n-ZnO/p-Si heterojunction diodes fabricated by pulsed laser deposition at different oxygen pressures. These heterojunction diodes are found to have highly favorable forward to reverse current ratio. We have also studied the parametric dependence of the electrical characteristics of these heterojunctions. The results of these studies are presented and discussed in this chapter.

4.2. Experimental

The pulsed laser deposition (PLD) of the ZnO films was carried out in a growth chamber, which was first evacuated to a base pressure of 10⁻⁶ mbar. Polycrystalline, stoichiometric, sintered (for 5 hours at 1200°C) pellet of ZnO with a purity of 99.999% was used as the target for PLD. The third harmonics (355 nm) of a Q-switched Nd: YAG laser with repetition rate of 10 Hz, pulse width of 9 ns and fluence of about 3 J/cm² per pulse was used for ablation of the ZnO target. P-type silicon wafers with (100) orientation and carrier concentration 1 x 10¹⁵ cm⁻³ were used as substrates. The silicon substrates were degreased in trichloroethylene (TCE), rinsed in de-ionized water, etched in a mixture of HF and H₂O (1:1) at room temperature for 5 minutes, and rinsed in TCE again. The growth chamber was filled with flowing oxygen ambient and its pressure was varied from 0.003 to 0.007 mbar during the growth of different samples. The substrate to target distance was kept about 4.5 cm. The ZnO films were deposited for about 30 minutes on the Si substrates at room temperature. To measure the conductivity and band gap of the ZnO films, those were
separately deposited on silica substrates under the identical experimental conditions as those used for the growth on the Si substrates. For electrical measurements, indium metal contacts were made on both p-type silicon surface and n-type ZnO films, which were found to be ohmic in nature. The room temperature electrical measurements of the ZnO thin films grown on the silica substrates were carried out using four probe van der Pauw configuration in hall geometry.

4.3. Results and discussion

Thickness of the deposited ZnO films, measured using a stylus profiler (Dektak 6M Stylus profiler) was found to be about 250 nm. X-ray diffraction pattern of all the ZnO films showed only (002) peaks along with that of the Si (200) peak. A typical XRD pattern of these films is shown in figure 4.1(a). This confirmed a highly c-axis oriented growth of the ZnO films. The full width at half maximum (FWHM) of the (002) x-ray diffraction peak of the ZnO films was found to be about 0.34°, indicating reasonably good crystalline quality of these films. X-ray diffraction pattern of the ZnO films deposited on the silica substrates is shown in figure 4.1(b). This also showed only a (002) peak of ZnO confirming the same c-axis oriented growth as in the case of ZnO films grown on p-Si substrates. However the FWHM of this peak was found to be about 0.36°, which is slightly higher than that of the films grown on the Si substrates as expected.
Figure 4.1 XRD pattern of ZnO films deposited on (a) p-silicon (100) and (b) silica substrates.

Figure 4.2 shows the $(\alpha h\nu)^2$ vs. $h\nu$ plot of ZnO films grown on silica substrates at different oxygen pressures. Figure 4.3(a) shows the variation of band gap of the ZnO thin films grown on silica substrates, estimated from $(\alpha h\nu)^2$ vs. $h\nu$ plot. It can be seen from this figure that the band gap decreased from 3.36 to 3.257 eV with increase of oxygen pressure from 0.003 to 0.007 mbar. Series resistance, an inherent resistance of the depletion region in n-ZnO/p-Si heterojunction of all the diodes grown at different oxygen pressures was calculated from log (I) vs. V plots [28], which is also shown in figure 4.3(a). As can be seen in this figure the series resistance increased from $3.45 \times 10^5$ to $5.6 \times 10^5$ ohm with increasing oxygen partial pressure from 0.003 to 0.007 mbar. Figure 4.3(b) the variation of resistivity and the electron mobility for the ZnO thin films with respect to the oxygen pressure. It can be seen from this figure that while the resistivity increased, the mobility decreased when the oxygen pressure used during the deposition was increased. The hall measurements confirmed the n-type conductivity of the ZnO films.
Figure 4.2 The $(\alpha h\nu)$ vs. $h\nu$ plot of ZnO films grown on silica substrates at different oxygen pressures.
Figure 4.3 (a) The series resistance and the optical band gap variation with oxygen pressure and 2 (b) the plot of resistivity and mobility with oxygen pressure.
Using these Hall measurements, the carrier concentration was found to decrease from about $3.2 \times 10^{19} \text{ cm}^{-3}$ to $1.32 \times 10^{18} \text{ cm}^{-3}$ when the oxygen pressure was increased from 0.003 mbar to 0.007 mbar, which is shown in figure 4.4. A theoretical curve based on the calculated values of the carrier concentration from the Burstein-Moss (BM) shift [29] is also shown in this figure. With a small gap between the two curves, the trend of experimental data and that of the calculated ones coincide reasonably well.

As seen from figure 4.3(a) band gap of the ZnO films decreased with increase of the oxygen pressure during their growth and so did the electron concentration. This means the films grown at lower oxygen pressure had higher band gap due to the enhanced carrier concentration in the film. Increase in the band gap accompanied by the enhanced carrier concentration can be explained using the BM shift [29]. As it is well known, this model relies on effective mass approximation (EMA), the wave functions are represented by plane waves and conduction band and valance band are taken to be parabolic near the Brillouin zone. The BM shift in band gap, $\Delta E_g$, according to this model [29] is given by:

$$\Delta E_g = \frac{\hbar^2}{8\pi^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \left(3\pi^2 n\right)^{2/3} \tag{4.1}$$

where $m_e = 0.28 \text{ m}_e$, $m_h = 0.59 \text{ m}_e$, are the effective electron mass, effective hole mass; $\hbar$ and $n$ are Planck constant and electron density per unit volume respectively.
This leads to a total band gap of

\[ E_g = E_{go} + \Delta E_g \]  \hspace{1cm} (4.2)

We took the band gap of ZnO without BM shift as \( E_{go} = 3.25 \text{ eV} \), which is that of the ZnO bulk crystal at room temperature [30]. BM shift in band gap (\( \Delta E_g \)) was obtained from equation (4.2) using the total band gap (\( E_g \)) estimated from the optical transmission spectra. Then electron concentrations (n) were calculated using the equation (4.1). These calculated values of electron concentrations are plotted as a function of the oxygen partial pressure in figure 4.4.

**Figure 4.4** The variation of electron concentration in ZnO films (obtained from the Hall measurement and theoretical model using BM shift) with oxygen pressure.
Experimental values of the electron concentrations obtained from the Hall measurements are also shown in figure 4.4. It can be seen in this figure that the electron concentrations obtained from Hall measurements match well with those obtained from the theoretical BM shift except for the lowest oxygen pressure. This might be due to the strain resulting from the increased oxygen vacancies in the film. Values of series resistance of the p-Si/ZnO heterojunctions, electron density (both calculated and experimentally observed) and band gap ZnO films are summarized in the table 4.1.

Table 4.1 The values of various observed and calculated parameters.

<table>
<thead>
<tr>
<th>Variation of Oxygen pressure (x 10^3 mbar)</th>
<th>Band gap (eV) calculated from absorption spectra</th>
<th>Electron density from Hall measurements (cm(^3) x 10(^{19}))</th>
<th>Electron density calculated using BM shift (cm(^3) x 10(^{19}))</th>
<th>Series resistance across the P-Si/ZnO heterojunction (x 10^6 ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>3.26</td>
<td>0.13</td>
<td>0.072</td>
<td>5.6</td>
</tr>
<tr>
<td>6</td>
<td>3.28</td>
<td>0.256</td>
<td>0.19</td>
<td>5.2</td>
</tr>
<tr>
<td>5</td>
<td>3.29</td>
<td>0.421</td>
<td>0.3</td>
<td>4.9</td>
</tr>
<tr>
<td>4</td>
<td>3.32</td>
<td>0.81</td>
<td>0.69</td>
<td>4.1</td>
</tr>
<tr>
<td>3</td>
<td>3.36</td>
<td>3.2</td>
<td>1.36</td>
<td>3.45</td>
</tr>
</tbody>
</table>
The physical basis for the concentration of oxygen incorporation in the ZnO films was investigated by x-ray photoelectron spectroscopy (XPS) of the films grown at oxygen pressures 0.003 and 0.007 mbar using Al Kα radiation source (1486.6 eV). The results are shown in figure 5. XPS of oxygen 1s peak intensity shows higher oxygen incorporation in the ZnO films grown at 0.007 mbar of oxygen pressure. It was also observed from the XPS data that increase of oxygen pressure during deposition enhanced the O/Zn ratio in the ZnO thin films. From the XPS and Hall measurement data it can be elicited that more the oxygen incorporation in the films lesser the electron concentration. This is also in conformation with the earlier study of Look et al [31].

Figure 4.5. XPS of O 1s ZnO thin films deposited at 0.007 mbar and 0.003 mbar oxygen pressures.
Figure 4.6 shows the J-V characteristics of five different n-ZnO/p-Si heterojunctions with ZnO films grown at different oxygen pressures. All the five heterojunctions were found to be rectifying and the turn-on voltage of the heterojunctions increased as shown in the inset of figure 4.6 with increase of oxygen pressure during the growth of the ZnO films. J-V characteristics of the n-ZnO/p-Si heterojunction diode with the lowest turn-on voltage is plotted on a logarithmic scale, which is shown in figure 4.7. Maximum forward to reverse current ratio is found to be about 1000 in the range of the applied voltage from -5 V to +5 V. Inset of the figure 4.7 shows the ohmic nature of In/ZnO contact.
Room temperature leakage current at -5 V is of the order of $10^{-7}$ A. The ideality factor was found to be greater than 10 for all the heterojunctions fabricated.

**Figure 4.7** Current density–voltage (J-V) plot of ZnO/p-Si heterojunctions on logarithmic scale. Inset shows the current-voltage (I-V) plot of In/ZnO contact.

Band structure of n-ZnO/p-Si at the heterojunction can be constructed using Anderson model [32] by assuming continuity of vacuum levels, neglecting the effects of dipole and interfacial states. Similar band structure has been suggested for doped and pure ZnO/Si heterojunction by P Chen et al [26,33]. Figure 4.8(a) and 4.9 show the constructed band structure of n-ZnO/p-Si heterojunction fabricated at 0.007 mbar oxygen pressure under zero bias and forward bias respectively. Values of band gaps $E_g$ (ZnO) = 3.257 eV and $E_g$ (Si) = 1.12 eV, electron affinities, $\chi$ (ZnO) = 4.35 eV and $\chi$ (Si) = 4.05 eV were
used [26]. Valance band offset (ΔEV) and conduction band offset (ΔEc) are equal to 2.43 eV and 0.3 eV respectively. Variation of ΔEv with oxygen pressure during PLD of ZnO films is shown in the figure 4.8(b). Both ΔEv and ΔEc are emerging out of the difference in the electron affinities and band gaps of two materials forming the junction. It can be noted that valance band offset ΔEv is much higher than conduction band offset ΔEc.

Figure 4.8 (a) The band structure of ZnO/p-Si heterojunction (grown at 0.007 mbar oxygen pressure) under zero bias and (b) shows the variation of ΔEv with oxygen pressure during PLD of ZnO films.
Since carrier concentration in the p-Si side is about 3 orders of magnitude lower than that in ZnO side, all the depletion region within the p-Si/ZnO heterojunction is extended into the p-Si side. Figure 4.8(a) shows that bottom of the conduction band on the ZnO side lies quite lower in energy than that on the p-Si side. Hence under relatively low forward bias, chance of electron flow from ZnO side to the p-Si side is negligible due to the higher barrier difference felt by the electrons in the bottom of the conduction band on the ZnO side. This resulted in higher turn-on voltage for p-Si/ZnO junction grown at 0.007 mbar of oxygen pressure. But under higher forward bias, the barrier difference lowered and the injection of electrons from the bottom of the conduction band on the ZnO side to the p-Si increased considerably (as shown in figure 4.9). Thereby forward current increased rapidly.

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**Figure 4.9** The band structure of ZnO/p-Si heterojunction (grown at 0.007 mbar oxygen pressure) under forward bias.
under higher voltage bias. When the oxygen pressure during the deposition of ZnO decreased, carrier concentration increased and hence Fermi level shifted towards the bottom of the conduction band. That means upon the decrease of oxygen pressure, Fermi level may even get into the conduction band and result in the ease of flow of electrons from ZnO side to p-Si side. Hence forward voltage required for considerable forward current decreased and there by turn-on voltage decreased. This seems to explain the decrease of the turn-on voltage for the n-ZnO/p-Si heterojunction fabricated at the lower oxygen pressure.

Variation of turn-on voltage with oxygen pressure can also be explained with calculated values of series resistance. Due to series resistance, effectively a part of the applied voltage is dropped and hence larger applied voltage is necessary to achieve the same level of current compared to the ideal one. Hence the turn-on voltage will be increasing with the increase of series resistance in the quasineutral region of p-Si/ZnO. It is noticed that calculated values of series resistance thus obtained increased with increase of oxygen pressure and thereby increasing the turn-on voltage.

4.4. Conclusion

In conclusion c-axis oriented crystalline ZnO films deposited on p-type Si (100) at different oxygen pressures using PLD form effective n-ZnO/ p-Si heterojunctions, which were found to be rectifying. Maximum forward to reverse current ratio was found to be 1000 in the applied voltage range from -5 V to +5 V. Variation of the turn-on voltage with oxygen pressure was modeled with Anderson model and BM shift which is in conformity with the values of series resistance calculated across the n-ZnO/p-Si heterojunction.
4.5. References