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   Electrical Characteristics of n-ZnO/p-Si Heterojunction Diodes Grown by Pulsed Laser Deposition at Different Oxygen Pressures

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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. These heterojunctions were found to be rectifying with a maximum forward-to-reverse current ratio of about 1,000 in the applied voltage range of −5 V to +5 V. The 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.

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Electrical Characteristics of n-ZnO/p-Si Heterojunction Diodes Grown by Pulsed Laser Deposition at Different Oxygen Pressures

R.S. AJIMSHA, 1 M.K. JAYARAJ, 1,3 and L.M. KUKREJA 2

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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. These heterojunctions were found to be rectifying with a maximum forward-to-reverse current ratio of about 1,000 in the applied voltage range of –5 V to +5 V. The 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.

Key words: Heterojunctions, ZnO, p-Si, pulsed laser deposition

INTRODUCTION

Currently there is significant interest in ZnO as a candidate for various future 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 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 diodes, 5–7 thin-film transistors, 8 multiple-quantum-well structures, 9 and solar cells. 10 Recently we have reported ZnO based all-transparent conducting p–n heterojunction diodes 11 with p-type AgCoO 2. 12 Although ZnO films can be grown by a variety of methods, including radiofrequency (RF) and direct-current (DC) sputtering, 3,13,14 chemical vapor deposition, 15 spray pyrolysis, 16 and electron cyclotron resonance-assisted molecular-beam epitaxy, 17 we used pulsed laser deposition (PLD) 18 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 the 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 dopants in the 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 the n-ZnO/p-Si heterojunction, the transport properties of these heterostructures are not yet well understood and are 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 communication.

(Received August 15, 2007; accepted December 3, 2007)
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. A polycrystalline, stoichiometric, sintered (for 5 h 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 a repetition rate of 10 Hz, pulse width of 9 ns, and fluence of about 3 J/cm$^2$ per pulse was used for ablation of the ZnO target. Cleaned $p$-type silicon (100) wafers with a carrier concentration of about $1 \times 10^{15}$ cm$^{-3}$ were used as substrates. The growth chamber was filled with flowing oxygen ambient and its pressure was varied from 0.003 mbar to 0.007 mbar during the growth of different samples. The substrate-to-target distance was kept at about 4.5 cm. The ZnO films were deposited for about 30 min 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 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 the four-probe van der Pau configuration in the Hall geometry.

RESULTS AND DISCUSSION

The thickness of the deposited ZnO films, measured using a stylus profiler (Dektak 6 M Stylus profiler) was found to be about 250 nm. The X-ray diffraction patterns of all the ZnO films showed only (002) peaks along with the Si (200) peak. A typical XRD pattern of these films is shown in Fig. 1a. This confirmed the 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 a reasonably good crystalline quality of these films.

![X-ray diffraction pattern of the ZnO films deposited on the silica substrates is shown in Fig. 1b. 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 the $p$-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.](image)

Figure 2a shows the band gap of the ZnO thin films grown on silica substrates, estimated from the plot of $(\alpha h v)^2$ versus $h v$. It can be seen from this figure that the band gap decreased from 3.36 eV to 3.257 eV with an increase of the oxygen pressure from 0.003 mbar 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 the plot of log ($I$) versus $V$, which is also shown in Fig. 2a. As can be seen in this figure the series resistance increased from $3.45 \times 10^5$ ohm to $4.0 \times 10^5$ ohm.
5.6 \times 10^5 \text{ohm} with increasing oxygen partial pressure from 0.003 mbar to 0.007 mbar. Figure 2b shows 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. Hall measurements confirmed the $n$-type conductivity of the ZnO films.

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, as shown in Fig. 3. A theoretical curve based on the calculated values of the carrier concentration from the Burstein-Moss (BM) shift\cite{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 Fig. 2a the band gap of the ZnO films decreased with increasing oxygen pressure during growth, as did the electron concentration. This means that films grown at lower oxygen pressure had a larger band gap due to the enhanced carrier concentration in the film. The increase in the band gap accompanied by an enhanced carrier concentration can be explained using the BM shift.\cite{29} As is well known, this model relies on the effective mass approximation (EMA) in which the wavefunctions are represented by plane waves and the conduction and valence bands are taken to be parabolic near the Brillouin zone. The BM shift in band gap, $\Delta E_g$ according to this model\cite{29} is given by:

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

where $m_e = 0.28 m_o$, $m_h = 0.59 m_o$, $\hbar$, and $n$ are the effective electron mass, effective hole mass, 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} (2)

We took the band gap of ZnO without BM shift to be $E_{go} = 3.25$ eV, which is that of the ZnO bulk crystal at room temperature.\cite{30} The BM shift in the band gap ($\Delta E_g$) was obtained from Eq. 2 using the total band gap ($E_g$) estimated from the optical transmission spectra. Then electron concentrations ($n$) were calculated using Eq. 1. These calculated values of the electron concentration are plotted as a function of the oxygen partial pressure in Fig. 3. Experimental values of the electron concentrations obtained from the Hall measurements are also shown in Fig. 3. It can be seen in this figure that the electron concentrations obtained from the Hall measurements match well with those obtained from the theoretical BM shift except at the lowest oxygen pressure. This might be due to the strain resulting from the increased oxygen vacancies in the film.

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 of 0.003 mbar and 0.007 mbar using an Al K$_\alpha$ radiation source (1486.6 eV). The results are shown in Fig. 4. The intensity of the oxygen 1s XPS peak showed greater oxygen incorporation in the ZnO films grown at 0.007 mbar 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, the greater the level of oxygen incorporation in the films, the lower the electron concentration. This is also in agreement with the earlier study of Look et al.\textsuperscript{31}

Figure 5 shows the $J$–$V$ characteristics of five different $n$-$ZnO/p$-$Si$ heterojunctions with ZnO films grown at different oxygen pressures. All of the five heterojunctions were found to be rectifying and the turn-on voltage of the heterojunctions increased as shown in the inset of Fig. 5 with increasing oxygen pressure during the growth of the ZnO films. The $J$–$V$ characteristics of the $n$-$ZnO/p$-$Si$ heterojunction diode with the lowest turn-on voltage is plotted on a logarithmic scale in Fig. 6. The maximum forward-to-reverse current ratio was found to be about 1,000 in the range of applied voltage from $-5$ V to $+5$ V. The inset to Fig. 6 shows the ohmic nature of the In/ZnO contact. The room-temperature leakage current at $-5$ V was of the order of $10^{-7}$ A. The ideality factor was found to be greater than 10 for all the heterojunctions fabricated.

The band structure of $n$-$ZnO/p$-$Si$ at the heterojunction can be constructed using the Anderson model\textsuperscript{32} by assuming continuity of vacuum levels and neglecting the effects of dipole and interfacial states. A similar band structure has been suggested for doped and pure ZnO$/$Si heterojunction by P Chen et al.\textsuperscript{26,33} Figures 7a and 8 show the constructed band structure of the $n$-$ZnO/p$-$Si$ heterojunction fabricated at the 0.007 mbar oxygen pressure under zero and forward bias, respectively. Values of the band gaps of $E_g$ ($ZnO$) = 3.257 eV and $E_g$ ($Si$) = 1.12 eV, and of the electron affinities of $\chi$ ($ZnO$) = 4.35 eV and $\chi$ ($Si$) = 4.05 eV, were used.\textsuperscript{26} The valance-band offset ($\Delta E_v$) and conduction-band offset ($\Delta E_c$) are equal to 2.43 eV and 0.3 eV.

![Fig. 5. Current density–voltage ($J$–$V$) plot of ZnO/p-Si heterojunctions. The inset shows the variation of the turn-on voltage with oxygen pressure, $P(O_2)$.](image)

![Fig. 6. Current density–voltage ($J$–$V$) plot of ZnO/n-Si heterojunctions on a logarithmic scale. The inset shows the current–voltage ($I$–$V$) plot of the In/ZnO contact.](image)

![Fig. 7. (a) The band structure of the ZnO/p-Si heterojunction (grown at 0.007 mbar oxygen pressure) under zero bias. (b) The variation of $\Delta E_v$ with oxygen pressure during PLD of ZnO films.](image)
The variation of the turn-on voltage with oxygen pressure during PLD of ZnO films is shown in Fig. 7b. Both $\Delta E_v$ and $\Delta E_c$ are emerging out of the difference in the electron affinities and band gaps of the two materials forming the junction. It can be noted that the valence-band offset $\Delta E_v$ is much higher than the conduction-band offset $\Delta E_c$.

Since the carrier concentration in the p-Si side is about 3 orders of magnitude lower than that in the ZnO side, all the depletion region within the p-Si/ ZnO heterojunction is extended into the p-Si side. Figure 7a shows that the bottom of the conduction band on the ZnO side lies lower in energy than that on the p-Si side. Hence under relatively low forward bias, the chance of electron flow from the ZnO side to the p-Si side is negligible due to the higher barrier difference felt by the electrons at the bottom of the conduction band on the ZnO side. This resulted in a higher turn-on voltage for the p-Si/ZnO junction grown at 0.007 mbar oxygen pressure. However, under higher forward bias, the barrier difference is 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 Fig. 8).

Thereby the forward current rapidly increased under a higher voltage bias. When the oxygen pressure during the deposition of ZnO was decreased, the carrier concentration increased and hence the Fermi level shifted towards the bottom of the conduction band. This means that, upon decrease of the oxygen pressure, the Fermi level may even move into the conduction band, resulting in the easy flow of electrons from the ZnO side to the p-Si side. Hence the forward voltage required for considerable forward current decreased and thereby the 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.

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

**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. The maximum forward-to-reverse current ratio was found to be 1000 in the applied voltage range from −5 V to +5 V. The variation of the turn-on voltage with oxygen pressure was modeled with the Anderson model and the BM shift, which is in agreement with the values of the series resistance calculated across the n-ZnO/p-Si heterojunction.

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**REFERENCES**