Current Transport Studies of n-ZnO/p-Si Hetero-Nanostructures Grown by Pulsed Laser Deposition

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ABSTRACT

In this work, the influence of Al<sub>2</sub>O<sub>3</sub> doping on ZnO thin films is reported in this study. The ZnO thin films were prepared on p-type Si. substrates by Q-switch second harmonic Nd:YAG laser deposition technique with wavelength of (532) nm and laser fluence energy density 0.6 J/cm<sup>2</sup> from a ZnO target mixed with Al<sub>2</sub>O<sub>3</sub> of (0-5) wt.%, and the films deposited at temperature (200°C). The transport properties of the undoped-ZnO/ p-Si and the Al<sub>2</sub>O<sub>3</sub>-doped-ZnO/ p-Si diodes were explained in terms of the Anderson model and the space charge limited current model, respectively. The spectral photoresponse and I-V characterization properties show the detector is a promise candidate for UV detection. High performance rectifying was obtained, with maximum responsivity of the ZnO/p-Si were 4.71 A/W at 340 nm, which corresponds to a external quantum efficiency of 99.64 %, for a given bandwidth of 50Hz and 5V applied bias. The results show that ZnO on silicon structures p-type will act as good candidates for making highly efficient photocurrent.

Key words: Al<sub>2</sub>O<sub>3</sub>-doped-ZnO/ p-Si nanostructures, I-V characterization, PLD, responsivity.

1. INTRODUCTION

Zinc oxide is a direct wide-band-gap semiconductor with a band-gap of 3.37 eV, coupled with a large exciton binding energy of 60 meV (at room temperature) [1]. ZnO is suitable for use in a wide range of optical and electronic applications. It is also notable that ZnO is biocompatible and exhibits high mechanical, thermal, and chemical stability. Thus, a wide range of applications includes, among others, biosensors, optoelectronic, solar cells, water photoelectrolysis and gas sensors [2,3]. The n-ZnO/p-Si heterojunction is not only more cost-effective for device fabrication but also promising for the integration with silicon microelectronic devices. In the ZnO:Al/p-Si heterojunction, the Al-doped ZnO (AZO) film was deposited on p-Si substrates as a practical photo-window as well as a semiconducting layer, causing a depletion region in the p-n heterojunction. In addition, the AZO contact layer can efficiently enhance the photoresponse of the heterojunction due to its metal-like property [4]. However, little research on this type of heterojunction has been reported [5]. It is important to understand the physical properties and the transport mechanisms of the AZO based devices prior to applications. However, ZnO, an n-type wide-band-gap semiconductor naturally generated due to oxygen deficiencies and interstitial Zn ions acting as donors in the ZnO lattice, can be a potential material for the fabrication of wide-band-gap p-n heterojunction when integrated with alumina film. For the fabrication of the heterojunction, the deposition of n-type ZnO films on the alumina-doped p-type silicon substrate has been prepared successfully [6], while few studies involved in n-ZnO/p- doped silicon heterojunction have been reported. The silicon film was very attractive for many industrial applications due to the similar properties to the film [7,8]. In this work, a p-type silicon film was deposited on a polycrystalline silicon substrate by doped method, and an n-ZnO film was then grown on this alumina film by pulsed laser deposition method to fabricate an n-ZnO/p-Si heterojunction. The I-V characteristic of the heterojunction was reported. The electrical characters of the sample films were studied and the physics of carrier transport was investigated in detail.

2. EXPERIMENT

The thin ZnO:Al<sub>2</sub>O<sub>3</sub>/p-Si polycrystalline films were prepared by employing pulsed laser deposition experiment under vacuum conditions (10<sup>-3</sup> Torr). Nd:YAG laser (Huafei Tongda Technology—DIAMOND-288 pattern EPLS) is used for the deposition of ZnO on different substrate. The whole system is consisting of light route system, power supply, computer controlling and cooling systems. The light route system is installed into the hand piece, while the power supply, controlling and cooling system are installed into the machine box of power supply.

X-ray diffraction (XRD) was employed to detect the effect of various deposition conditions on the crystallization behavior of the investigated thin films. The X-ray diffraction patterns of the ZnO thin films were recorded with a Philips PW 1840 using CuKα radiation (1.54056) operating at a target voltage and current of 40kV and 30mA, respectively with Ni filter. The spectra were obtained by scanning 2θ within the range of 25°- 38°. Diffraction peaks are recorded, showing phases
present (peak positions) and phase concentrations (peak heights), and the corresponding interplaner spacings ($d_{hkl}$Å) and the relative intensities ($I_{hkl}$) are determined and compared with value in the American Standard for Testing Materials (ASTM) cards for ZnO. The microstructures of the films were analyzed using Scanning Electron Microscope, (SEM, JEOL JED 2300) and by Atomic Force Microscopy (AFM-Digital Instruments Nan Scope) working in tapping mode.

Dark and light ($I$-$V$) measurements were done by using a Keithley- 616 digital electrometer and Tektronix CDM 250 multimeter. Spectral photoresponsivity measurements were carried out using a light source and a monochromator with spectral range (300-1200) nm. Spectral responses of the fabricated ZnO:Al$_2$O$_3$ nanostructures PD to a 300-W Xe lamp dispersed by a monochromator used as the excitation source. During these measurements, the monochromatic light was calibrated by a UV-enhanced pSi diode, and an optical power meter was modulated by a mechanical chopper and collimated onto the front side (i.e., the metal side) of the fabricated devices using an optical fiber. The photocurrent was then recorded by a lock-in amplifier.

3. RESULTS AND DISCUSSION

The heterojunction band structure of the undoped-ZnO/ p-Si can be constructed by the Anderson model (9) [9]. Values of electron affinity of $\chi$ZnO=4.4 eV and $\chi$Si=4.6 eV band gaps of $E_g$ (ZnO)=3.4 eV and $E_g$ (Si)=1.1 eV were taken. The band structure of such a heterojunction is shown in Figure 1. As shown in Fig. 1, the barrier for electron is equal to $\Delta E_C=\chi$ZnO $- \chi$Si = 0.3 eV and that for hole is equal to 2.8 eV. Both the conduction band and the valance band have band offsets which are originated from the difference in the electron affinities and the band gaps of the two materials. It is noticed that the valance band offset $\Delta E_V$ is much larger than the conduction band offset $\Delta E_C$. As the carrier concentration of the p-Si is much lower than that of the undoped ZnO, the depletion space charge region mainly locates at the p-Si side. As the ZnO side is under the negative bias, the conduction band barrier will be decreased and will enhance the electron flow from the ZnO to the p-Si.

The subsequent recombination at the p-Si depletion region would give rise to the forward bias current flow. This implies that the diode resistance would firstly decrease upon the increase of the forward bias voltage (i.e., the lowering of the barrier). As the forward bias is large enough, the barrier would essentially be negligible, the $I$-$V$ behavior thus becomes Ohmic, and the diode resistance becomes constant, which is contributed from the series bulk material resistance.

![Figure 1](image.png)

**Figure 1** Band structure of the ZnO/ p-Si heterostructure derived from the Anderson model. [9]

Figure 2, illustrates the XRD patterns of ZnO films with various Al$_2$O$_3$ doping concentrations. Shows a XRD pattern (using 20 values in the range of (25°- 38°) taken on the top surface of the heterojunction, the dominant peak in the XRD pattern is the Si (111) peak (located at 2θ=28.25°), while the weak peak at 2θ =31.65°, 34.3° and 36.25°, is from the ZnO (100), (002) and (101) respectively orientation due to the minimal surface energy in the ZnO hexagonal wurtzite structure.

Diffraction of peaks is caused by the diffraction of Si (111). The XRD pattern indicates the highly oriented crystallographic growth of ZnO: Al$_2$O$_3$ films with c-axes perpendicular to the substrate surface. The intensity of the p/Si (111) peaks increase with increasing Al$_2$O$_3$-doping.

In addition, the location of the Si (111) peaks is shifted to higher 2θ angles, from 2θ=28.25° to 2θ=28.29° as Al$_2$O$_3$-doped content increases from 0 to 5 wt. %. [10].
Figure 2 XRD spectrum of ZnO pure and alumina-doped ZnO thin films deposited on Si substrate.

Figure 3 shows a SEM picture. The SEM picture (Figure 3) shows that the ZnO film consists of tightly packed grains with sizes in the (44-86 nm) range. There are significantly change in the morphology of ZnO film after the Al\textsubscript{2}O\textsubscript{3} doping. It is found that the Al\textsubscript{2}O\textsubscript{3} doping concentration has a significant influence on ZnO film surface structure, the grain size increases as the Al\textsubscript{2}O\textsubscript{3} concentration increases. The average grain sizes of the films with Al\textsubscript{2}O\textsubscript{3} of undoped, 5wt.\% are 44 and 86 nm, respectively. The average grain size (g.s) estimated from X-ray diffraction using the Scherrer’s formula calculated and is in the range of ~ (33 - 70) nm. Therefore, as shown in SEM surface micrograph the grain size is larger than that estimated from XRD data, this goes in agreement with the previous work [11].

Figure 3 SEM image of a ZnO: Al\textsubscript{2}O\textsubscript{3} film (thickness 100 nm) deposited onto a p-Si wafer, as the fluence laser energy is raised to 0.4 J/cm\textsuperscript{2}, T\textsubscript{sub}=200 °C and 10-2 mbar of oxygen gas.

Figure 4, shows AFM micrographs of ZnO thin films on Si (111) substrates at growth temperatures (200 °C). It is clear that a dense nano-order spike-type grain growth occurs at room temperature. The RMS roughness of the scanned surface area increased of 25.45 nm to 67.88 nm, as shown in table 1. The grains are oriented along the c direction, as confirmed by XRD data. Studies of the spontaneous ordering of semiconductor nanostructures established that long-range elastic interaction is the driving force for this ordering. In our case we can see small grains fused together to produce uniform big grains with an average size. Film thickness and deposition temperature control the size (base diameter) and height distribution of grains. When the dopant concentration is increased to (5w.t.\%) it is clear from the AFM images that the grain size increased and the RMS roughness of the films increased to 67.88 nm. The 3D-AFM right pictures of pure and dopant are shown in figure 4. From AFM images we found that the presence of the ZnO:Al\textsubscript{2}O\textsubscript{3} films increases the (RMS) roughness in the films figures. The higher of the root mean square (RMS) roughness is found for ZnO: Al\textsubscript{2}O\textsubscript{3} films which have compressive stress and lower root mean square (RMS) roughness for ZnO film which has tensile stress. [12, 13]

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS surface roughness (nm)</th>
<th>Mean Topography variation (nm)</th>
<th>Average deviation (nm)</th>
<th>Skewness</th>
<th>Kurtosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>25.45</td>
<td>31.51</td>
<td>13.95</td>
<td>4.36</td>
<td>26.54</td>
</tr>
<tr>
<td>Doped (5%)</td>
<td>67.88</td>
<td>151.38</td>
<td>49.97</td>
<td>1.73</td>
<td>3.42</td>
</tr>
</tbody>
</table>

Table 1: Topography Statistical characterization of ZnO: Al\textsubscript{2}O\textsubscript{3}/ p-Si by AFM.
Figure 4 Atomic force microscopy (AFM) of pure ZnO and Al₂O₃ doped ZnO films and deposited onto a p-Si.

Figure 5 and 6 shows current–voltage (I–V) characteristics of the fabricated ZnO: Al₂O₃ /p-Si photodiodes with Al electrodes measured in dark and under illumination. During photocurrent measurements, the wavelength of the excitation light was 340 nm while the incident optical power in case illumination was 2 mW and in case dark 4.4 µW. The forward and reverse dark current versus applied voltage (I-V) characteristics for ZnO:Al₂O₃ /p-Si heterojunctions deposited at temperature equal to RT at various doping percentage of Al₂O₃ in the ZnO thin film are shown in Figure 5. In general, the I-V curves of these heterojunctions under the forward bias condition and reverse bias show the exponential rise at low voltage (below 0.2 V). This is due to the decrease in the width of depletion region at the junction as a result of an increase in the majority carriers injected by the applied voltage which lead to the decrease in the built-in potential. As the bias is increased the forward current increases and the deviation from the exponential behavior is highlighted in these figures. At higher voltage the I-V dependence are linear due to the influence of appreciable series resistance on the junction characteristics [14]. Also it can be seen from this figure that for ZnO:Al₂O₃/p-Si heterojunctions deposited at RT, the forward current increases with increasing doping percentage (1-5) % of Al₂O₃ in ZnO thin film. These may be due to the increase of carrier concentration which affected the energy band bending and thus result in a decrease in depletion region width.

Figure 5 I-V characteristic of the undoped-ZnO/ p-Si and the Al₂O₃-doped-ZnO/ p-Si-Dark heterojunction measured at room temperature.

The current-voltage characteristics under illumination are one of the optoelectronic characteristic for heterojunction. The photocurrent is considered as an important parameter that plays an effective role in solar cell devices. From the previous investigation, it has been selected some of heterojunctions which are possessed more sensitivity to illumination than the other heterojunctions. The current-voltage characteristics under illumination of the selected heterojunctions are shown in Figure 6, for ZnO:Al₂O₃/p-Si. It is observed that, in general, as mentioned previously the forward I-V characteristics in dark of these heterojunctions show an exponential behavior. Upon illumination of the junction, more carriers are generated and forward current increases. It is seen that the illuminated forward current increases with increasing the incident light intensity and with increasing the bias voltage. Also it is clear that illuminating the junctions increased the
reverse bias current as expected from the electron-hole pair generation in the depletion region if the incident photon energy is greater than the smallest direct band gap of the heterojunction [15].

Figure 6 I-V characteristic of the undoped-ZnO/ p-Si and the Al₂O₃-doped-ZnO/ p-Si-Light heterojunction measured at room temperature.

Semilogarithmic plots of the forward dark current versus applied voltage for undoped and doped Al₂O₃ heterojunctions deposited at RT are shown in Figure 7. These plots can be classified into one region corresponding to the applied voltage for ZnO:Al₂O₃/p-Si heterojunction. Also these figure show that in general, the reverse saturation current (Iₛ) increases with the increasing doping percentage Al₂O₃ in the ZnO thin film. This behavior is in agreement with Wary et al. [16]. Table 1, listed the values of ideality factor (β) for ZnO:Al₂O₃/p-Si heterojunctions at different doping percentage for ZnO:Al₂O₃ thin film which deposited at RT. The result in Table 1 shows that the value of β for undoped is 2.27 decreases from 1.98 to 1.62 upon increase with Al₂O₃ percentage. The ideality factor (β) has been calculated using equation 1. [17]:

\[
\beta = \frac{q}{k_B T} \frac{dV_f}{d[I_f / I_s]} \tag{1}
\]

Where:
- q: is the electronic charge (C).
- k_B: is the Boltzmann constant (J/K).
- T: is the temperature (K).
- I_s: is the saturation current and it can be obtained by extrapolating the forward current curves to zero voltage.
- I_f: is the forward current (A).
- V_f: is the forward bias voltage (V).

Figure 7 Semilogarithmic plot of forward bias of dark I-V curves for ZnO /p- Si heterojunction at different doping percentage of Al₂O₃ and deposited at room temperature.

Table 2 Ideality factor values which obtained from I-V characteristics for pure ZnO, Al₂O₃ doped ZnO p-n heterojunction under dark.
Figure 8, show a semilogarithmic plot of the forward photo current versus applied voltage, general, the reverse saturation current increases with the increasing doping percentage to 5% for Al$_2$O$_3$ in the ZnO thin film. This behavior is in agreement with Figure 7 for forward dark current versus applied voltage. Also $\beta$ is found to increase for ZnO pure to 1.92, while the value of $\beta$ decreases with increasing doping percentage of Al$_2$O$_3$, as shown in table 3.

![Figure 8](image-url)

**Figure 8** Semilogarithmic plot of forward bias of Light I-V curves for ZnO/p-Si heterojunction at different doping percentage of Al$_2$O$_3$ and deposited at room temperature.

<table>
<thead>
<tr>
<th>Type of doping in ZnO</th>
<th>Ideality Factor ($\beta$)</th>
<th>Type of heterojunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>2.27</td>
<td>p</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (1%)</td>
<td>1.98</td>
<td>p</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (3%)</td>
<td>1.77</td>
<td>p</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (5%)</td>
<td>1.62</td>
<td>p</td>
</tr>
</tbody>
</table>

Spectral photoresponse measurements were done in the (300–1200nm) range, using a xenon lamp light source, a single-pass monochromator and a calibrated p/Si photodetector.

Figures 9 shows the measured spectral quantum efficiency of a ZnO:Al$_2$O$_3$/p-Si UV detector under reverse bias voltages ranging about 5V. The quantum efficiency decreased with increasing doping percentage of Al$_2$O$_3$, comparison with undoped thin films whereas it increases with undoped ZnO/p-Si and reached a maximum value of ~99% at 293nm for ZnO:Al$_2$O$_3$/p-Si under 5V reverse bias. The cutoff wavelength red shifted with doping Al$_2$O$_3$/p-Si, from 290 to 420 nm for 5V reverse bias, respectively. Since $\lambda c<500$nm was satisfied, true solar-blind detection was successfully demonstrated.

The corresponding device responsivity curve under 5V reverse bias is shown in Figures 9, a peak responsivity of 4.71 A/W at 340 nm for ZnO:Al$_2$O$_3$/p-Si is measured.

To estimate the detectivity ($D*$) of our detectors in the photovoltaic mode, we have used the thermal-noise limited detectivity relation: [32]

$$D^* = R_0 \left( \frac{R_0 A}{4KT} \right)^{1/2}$$

Where $R_0$ is the device responsivity at zero bias, $R_0$ is the zero volt dark impedance and $A$ is the detector area. With a 0.01 A/W photovoltaic responsivity at 250 nm, the zero-bias detectivity of our detectors were in excess of 6.75x10$^{13}$ cm Hz$^{1/2}$/W, which corresponds to a setup limited Noise Equivalent Power (NEP) of 8.7x10$^{-13}$ W/Hz$^{1/2}$ for ZnO:Al$_2$O$_3$/p-Si.
We can also calculate the quantum efficiency of our photodiodes from the measured spectra response by using equation 3:

\[ R_\lambda = \eta x \frac{q\lambda}{hc} \] ..............................(3)

Where:
\( \eta \) is the quantum efficiency, \( q \) is the electron charge, \( \lambda \) is the incident light wavelength, \( h \) is the Planck constant and \( c \) is the speed of light.

Finally, noise characterization of the solar-blind Schottky detectors were carried out in the frequency range of 1Hz – 50 kHz using a fast Fourier transform spectrum analyzer and a microwave probe station. Our low-leakage, high breakdown voltage solar-blind detectors had noise power densities below the instrument resolution. Even under reverse bias as high as 1V, the detector noise did not exceed the measurement setup noise floor of 3x10^{-29} A^2/Hz around 10kHz. Therefore, we have measured devices with higher leakage currents in order to observe the bias dependence of the spectral noise density. [18].
CONCLUSIONS

Thin films of Al$_2$O$_3$ have been deposited on to the p/Si substrate by PLD in 10$^{-3}$ mbar O$_2$ ambient at different alumina concentration with laser fluency energy 0.6 J/cm$^2$. It was found that doped ZnO films with good structural and morphological properties can be deposited at 5%. The film deposited at an optimum alumina concentration 5% exhibited less intensity and FHWM with average grain size of (33-70nm) for XRD, as shown in SEM surface micrograph the grain size is larger than that estimated from XRD data maintaining average RMS roughness of (~25.45-67.88 nm). The $I$–$V$ characteristics of the sample measured in dark and under illumination condition prove that this structure has properties of a semiconductor junction and exhibits strong photocurrent effect. The spectral response of photocurrent indicates that this effect mainly relates to the structure of energy level in ZnO film. In conclusion, demonstrated solar-blind based Schottky photodiodes with low dark current, low noise, and high detectivity. Breakdown voltages larger than 5V reverse bias were achieved. Device responsivities as high as 4.71 A/W at 340 nm for ZnO:Al$_2$O$_3$/p-Si were measured under 5V reverse bias. Detector noise was 1/f limited with spectral noise density values less than of $8.7 \times 10^{-13}$ W/Hz$^{1/2}$ for ZnO:Al$_2$O$_3$/p-Si under reverse bias voltages as high as 4V.

References