Structural, Morphological, Photo-Properties of Heterojunction ZnO Nanostructure Films Deposited on n-Si(100) by PLD

Ali Ahmed Yousef
Department of Physics, College of Education, University of Al-Mustansiriyah, Baghdad, Iraq

ABSTRACT

In this work, Zinc oxide (ZnO) undoped and doped ZnO thin films with various dopant percentage (Co & Al2O3) and their heterojunctions which deposited on (100) n-type Si substrate and investigate their physical properties such as structural, optical, electrical and optoelectronic properties. Nanostructure films were prepared by Pulsed Laser Deposition (PLD) by Nd-YAG Q-switching second harmonic generation (SHG) Pulsed Laser with a wavelength of 532nm, repetition rate 10 Hz and pulsed width 10ns. The effect of doping on the physical properties of the ZnO pure and doped Co, Al2O3/n-Si nanostructure films have been investigated by X-Ray diffraction (XRD), scanning electron microscopy (SEM) and Atomic force microscopy (AFM). The result showed that crystalline and (100)-oriented thin films were obtained at all substrate temperature, laser fluence (1.6) J/cm² and the films grown at 400°C. The smallest grain size was obtained at ZnO pure are 31nm then increase upon increasing doping with Co, Al2O3.

I-V characteristics have measured in dark and under illumination. The dark and illumination forward and reverse current increases with increasing doping percentage Al2O3 and the tunneling is dominant transport mechanism in these heterojunctions. The ideality factor varies between ~ (1.1-2.5), the ratio between the forward and reverse current indicated that ZnO/n-Si heterojunction doped with Co, Al2O3 and deposited at RT have a good rectification property compared to the other heterojunctions. The responsivity results of ZnO/n-Si photodetectors for a xenon lamp light source revealed values equal to (0.09-0.33)A/W and (0.12-0.25)A/W that corresponding to the Co and Al2O3-content (1-5) wt.% respectively for (4V) bias voltage. High performance rectifying was obtained, with high photoresponsivity of 0.33 A/W at 320 nm for Co 3 wt.%. The outcomes of all these measurements indicate that such materials posses a good response to illumination which make it a candidate for heterojunction device used as basic for fabricating photo sensors.

Keywords: Pulsed-laser deposition, ZnO/n-Si heterojunction, I-V Characteristics, Spectral Measurements

1. INTRODUCTION

ZnO, due to its wide direct band gap (~3.3eV), large exciton binding energy (60meV), transparency in the visible range, non-toxicity, abundance in nature, is an excellent versatile II–VI compound semiconductor [1]. ZnO nanostructures, as a II–IV binary semiconductor, have attracted considerable attention because of their good optical, electrical and easily tunable morphological properties and their potential applications in solar cells, solar energy-hydrogen conversion devices, photo-electro chemical hydrogen generation applications and sensors [2]. However undoped ZnO thin films are not stable specially a thick temperatures, doping the zinc oxide can reduce this disadvantage. Besides, that doping leads to an increase in the conductivity of the ZnO thin films [3]. The ZnO doping is achieved by replacing Zn2+ atoms with atoms of elements such as aluminum [4], potassium [5] and cobalt [6]. The fundamental properties of defects, which behave as interstitials and vacancies in the ZnO system, are still unsolved problems. However various defects induced by doping are often observed in ZnO, which result in defects in the fundamental properties of ZnO films [7]. However in such applications, it is imperative to grow good quality thin films of ZnO especially on substrates of the most used electronic material, i.e., silicon (Si), albeit it is totally lattice mismatched. Many techniques have been used to synthesize thin films of ZnO. Pulsed laser deposition (PLD) technique has emerged as a viable technique for the growth of ZnO thin films due to its various advantages, viz., (i) the ability to reproduce the stoichiometry of the target materials under optimized deposition conditions, (ii) an inherently clean process with significant degree of parameter freedom, etc. In this study, the aim of present work is to utilize this Pulsed laser deposition (PLD) technique to prepare undoped and doped ZnO thin films with various dopant percentage (Co & Al2O3) and their heterojunctions which deposited on (100) n-type Si substrate and investigate their physical properties such as structural, optical, electrical and optoelectronic properties. The ultimate objective of our study is obtained a series of related results from measurements of different physical properties which we hope to be suitable for using them in various optoelectronic devices. Many investigations are still carried out to improve the characteristics of ZnO materials. However, to the best of our knowledge, there is no study which compares the effects of Co and Al2O3 dopants on morphological, structural, electrical...
and optical properties of ZnO. Thus, it is of interest to us to investigate the influence of the Co and Al₂O₃ dopant elements on the properties of ZnO thin films deposited by PLD method.

2. EXPERIMENT
ZnO pure and doped Co, Al₂O₃/n-Si nanostructure films sintered target of high–purity 99.99% was mounted in a locally design vacuum chamber and ablated by a double frequency with Q-switched Nd:YAG pulsed laser operated at 532 nm, pulse duration of about 10 ns, and a (1.6) J/cm² energy density was focused on the target to generate plasma plume. The target to substrate distance was (3cm). Targets of pure ZnO, Co and Al₂O₃-doped ZnO films (0-5wt.%) porcelain materials were prepared by sintering at the temperature of 10°C. Amorphous fused silica (commercial available from Alfa Aesar) was used as substrates thin films were grown in Oxygen environment with O₂ partial pressure of 10⁻² mbar, the deposition thin films were grown typically 10min after the deposition thin films were cooled to room temperature.

All samples were grown at an optimal substrate temperature of 400°C. The morphological features of the various films were investigated with a JEOL JSM-6360 equipped with an EDAX detector.

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 20 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 (dₜₜₜₜ)Å and the relative intensities (I/Iₚ) 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 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 monochrometer with spectral range (300-1200) nm. Spectral responses of the fabricated ZnO:Co and ZnO:Al₂O₃ nanostructure 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 n/Si 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

3.1. XRD ANALYSIS OF THE NANOSTRUCTURE UNDOPED AND Co DOPED ZnO FILMS
The X-ray diffraction patterns of undoped and Co doped ZnO nanostructure films are shown in figure (1). The peaks corresponding to Si and ZnO:Co films in figure are coming from the n-type silicon substrate. The results in Table (1) prove that the doping process in our study is almost successful.

As seen in the figure (1), all the films are polycrystalline and contain on silicon peak (111) and phase ZnO with hexagonal wurtzite structure without any other peaks which indicate that the Co has entered into ZnO lattice. This result is consistent with those of the Refs. [8]-[11] in which the Co doping did not change the wurtzite structure of ZnO films. For ZnO:Co films, all the observed peaks were indexed comparing with JCPDS data file [12]. It is seen that all the films have a (100) preferred orientation. Other orientations like (002) and (101) are also seen with comparatively lower intensities. As also seen in figure 1, the crystalline quality of ZnO film decreases with increasing cobalt content, which is due to the degradation of crystallinity. The occupation of the site of Zn²⁺ in the lattice by the Co ions may induce a crystal defect, resulting from the difference in ion size between zinc and cobalt.

Therefore, these defects change the stoichiometry of the ZnO lattice, furthermore, as a result of incorporation of Co ions into ZnO lattice, the crystal lattice distortion can also be induced. Decrease in the peak intensity with decrease in full width at half maxima (FWHM) observed in the XRD patterns of doped films confirm a decrease in crystalline quality depending on the cobalt content. For all the films, the grain size (D) given in Table (1) was calculated from the full width at half maximum (FWHM) of the (100) diffraction peak by using the Scherrer equation from [13]-[14]. It is seen from this table that Co doping causes FWHM (β) to decrease and grain size of the ZnO films to increase. In order to investigate the variation of the volume of the unit cell (V) and the lattice constants (a, b and c) of the hexagonal ZnO films with Co doping, we used the formulas in [15].

\[
\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2} \quad \text{and} \\
V = \frac{\sqrt{3}}{2} a^2
\]
It is concluded that the values given in table (1) almost agree with those of obtained from the ASTM card for polycrystalline ZnO powder of hexagonal structure [12]. The preferential growth orientation was determined using a texture coefficient $T_C(hkl)$. This factor is calculated using the following relation [16].

$$T_C(hkl) = \frac{[I(hkl)/I_o(hkl)]}{[Nr^{-1} \sum I(hkl)/I_o(hkl)]}$$  \hspace{1cm} (2)

Where $I(hkl)$ is the measured relative intensity of a plane (hkl), $I_o(hkl)$ is the standard intensity of the plane (hkl) taken from the JCPDS data, $Nr$ is the number of diffraction peaks. A sample with randomly oriented crystallite presents $T_C(hkl)=1$, while the larger this value is, the larger abundance of crystallites oriented at the (hkl) direction is. The texture coefficients calculated for the three main diffraction peaks, i.e. (100), (002) and (101), are presented in figure (1). It is seen that the highest $T_C$ values are in (100) plane for all the films. (100) orientations of all the films decrease while (002) and (101) orientations increase. The lattice parameter of a and c were calculated using analytical method for all the films [16]. These values are presented in Table (1). As seen in Table 1, the lattice parameters of the films do not change significantly with increase in Co content, which results from the fact that Co$^{2+}$ (0.58 Å) and Zn$^{2+}$ (0.60 Å) have almost identical ionic radii [17].

![XRD patterns of the nanostructure undoped and Co-doped ZnO films grown on the n-type silicon substrate](image)

**Table 1:** The volume of the unit cell (V), FWHM, grain size (D), Texture Coefficient ($T_C$) and the lattice constants (a, b and c) for the ZnO:Co/n-Si films.

<table>
<thead>
<tr>
<th>Texture Coefficient $T_C$ (h k l)</th>
<th>c (Å)</th>
<th>a = b (Å)</th>
<th>D (nm)</th>
<th>FWHM (β) deg</th>
<th>V (Å)$^3$</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.68</td>
<td>5.300</td>
<td>3.248</td>
<td>31</td>
<td>0.270</td>
<td>47.25</td>
<td>ZnO</td>
</tr>
<tr>
<td>1.39</td>
<td>5.216</td>
<td>3.248</td>
<td>33</td>
<td>0.254</td>
<td>46.5</td>
<td>ZnO:Co (1 at.%)</td>
</tr>
<tr>
<td>1.41</td>
<td>5.099</td>
<td>3.249</td>
<td>60</td>
<td>0.138</td>
<td>44.86</td>
<td>ZnO:Co (3 at.%)</td>
</tr>
<tr>
<td>1.32</td>
<td>5.210</td>
<td>3.250</td>
<td>69</td>
<td>0.120</td>
<td>46.68</td>
<td>ZnO:Co (5 at.%)</td>
</tr>
<tr>
<td>1.4</td>
<td>5.212</td>
<td>3.248</td>
<td>60</td>
<td>0.138</td>
<td>46.39</td>
<td>ZnO:Al$_2$O$_3$ (1 at.%)</td>
</tr>
<tr>
<td>1.44</td>
<td>5.205</td>
<td>3.258</td>
<td>70</td>
<td>0.119</td>
<td>46.6</td>
<td>ZnO:Al$_2$O$_3$ (3 at.%)</td>
</tr>
<tr>
<td>1.5</td>
<td>5.089</td>
<td>3.258</td>
<td>62</td>
<td>0.135</td>
<td>44.89</td>
<td>ZnO:Al$_2$O$_3$ (5 at.%)</td>
</tr>
</tbody>
</table>

### 3.2 XRD ANALYSIS OF THE NANOSTRUCTURE UNDOPED AND Al$_2$O$_3$ DOPED ZnO FILMS

Figure (2), shows the XRD patterns of pure and Al$_2$O$_3$ doped ZnO films with various doping concentrations. The position of the diffraction peaks was in good agreement with the Powder Diffraction Standard data (JCPDS data card 36-1451) indicated that all the films were polycrystalline with a structure that belonged to the hexagonal wurtzite type. No peaks corresponding to Al$_2$O$_3$ phases were detected. It is seen that all the films have a (100) preferred orientation. Other orientations like (002) and (101) are also seen with comparatively high intensities by the compared with ZnO:Co thin films.
The texture coefficient for the doped ZnO thin films was estimated from the following relation (2), a sample with randomly oriented crystallite yields $T_C \ (hkl) = 1$, while the larger this value, the larger abundance of crystallites oriented in the (hkl) direction [18]. The calculated texture coefficients $T_C$ are presented in Table 1. It can be seen that all the doped films exhibited larger value for the (100) plane and the value increased with increase in doping concentration. The mean crystallite size was calculated for the (100) plane diffraction peak by using the Scherrer formula [19].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

Where $k = 0.9$, $\lambda = 1.5405 \, \text{Å}$ and $\theta$ is the Bragg’s angle in degrees, $\beta$ is the full width at half maximum (FWHM) of the preferred orientation plane. The mean crystallite size alone the (100) plane increased as the Al$_2$O$_3$ doping concentration increased from 1 at.% to 3 at.%. However, when the concentration was above 3 at.%, reduction in the crystallite size was observed in the concentration of 5 at.% was the turning point. Both $T_C$ values and the crystallite size indicated that the structure of the doped ZnO films were quite dependent on the doping concentrations. The crystallite size, the full width at half maximum (FWHM) of pure ZnO and doped ZnO thin films were shown in Table 1. From Table (1), it was clear that the peak position corresponding to the (100) plane of AZO films was shifted to the higher value of the diffraction angle compared with pure ZnO thin films. Similar results had been reported previously [20]-[21].

This could be due to the change of intrinsic strain through doping, which causes the change of lattice constants [18]. The lattice constants $a$, $c$ and of the volume of the unit cell ($V$) was calculated by using the following equation (1) [22].

$$V = \frac{a \cdot b \cdot c \cdot \sin \gamma}{2}$$

![Figure 2 XRD patterns of the nanostructure undoped and Al$_2$O$_3$-doped ZnO films grown on the n-type silicon substrate](image)

**3.3 SEM ANALYSIS OF THE NANOSTRUCTURE UNDOPED AND Co, Al$_2$O$_3$ DOPED ZnO FILMS**

The surface morphology of the films was studied by SEM, and the top views SEM images taken at two different magnifications for pure and doping are shown in figure (3). At these figures, the effect of cobalt can be clearly seen and especially its effect on the crystallite size. As seen in figure (3), the crystallite size increases depending on the cobalt content. The same trend was also observed in the XRD results. In the SEM image of undoped ZnO, the nanocrystallite size is about between 30 and 70 nm and these nanocrystallites increases gradually with increasing cobalt content. Therefore, both increase in crystallite size and increase in the porosity of the films cause an decreases in density with the increase of Co content.

In case of doping with Al$_2$O$_3$ (figure (3)), it can be seen that, shows surface morphologies of AZO thin films with various doping Al$_2$O$_3$. It was quite clear that the surface nature of the films was greatly influenced by doping Al$_2$O$_3$. The surface morphology showed a closely packed arrangement of crystallites in both doped films. The grain size slightly increased when the doping concentration for Co, Al$_2$O$_3$ doped ZnO films, but at higher percentage it decreased was clearly seen in the micrographs, which were consistent with the XRD analyses. Larger grain size means better crystal quality. 3wt.% AZO thin films exhibited the maximum grain size [23] reported that larger grain size may due to the evolution of microstructure that small grain coalesced together to form larger grains related to the migration of surface atoms during the deposition. Similar results had been reported previously [22].
Figure 4. Atomic force microscopy (AFM) of pure ZnO and Co, Al₂O₃ doped ZnO films and deposited onto a n-Si

Table 2: Topography Statistical characterization of ZnO:Co and Al₂O₃/ n-Si by AFM

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS surface roughness (nm)</th>
<th>Mean Topography variation (nm)</th>
<th>Average deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>25.45</td>
<td>31.51</td>
<td>13.95</td>
</tr>
<tr>
<td>Doped Co</td>
<td>56.94</td>
<td>90.42</td>
<td>41.18</td>
</tr>
<tr>
<td>Doped Al₂O₃</td>
<td>67.88</td>
<td>151.38</td>
<td>49.97</td>
</tr>
</tbody>
</table>

4. I-V CHARACTERISTICS for THE NANOSTRUCTURE UNDOPED AND Co, Al₂O₃ DOPED ZnO FILMS HETEROJUNCTION IN THE DARK
The total dark current of the heterojunctions can be represented as a sum of several components such as generation-recombination current, diffusion current, tunneling current, surface leakage current, and emission current [25]. If generation-recombination and diffusion mechanisms are dominant, then the dark current (I) obeys the following formula [26].

\[ I = I_s \left[ \frac{\exp \left( \frac{qV}{\beta kT} \right) - I}{1 - I} \right] \]  

(4)

Where \( I_s \) is the saturation current, and \( \beta \) is the ideality factor having a value between 1.0 and 2.0 [25]. When the tunneling current is the dominant carrier transport mechanism.

The forward and reverse dark current versus applied voltage I-V characteristics for ZnO:Co/n-Si and ZnO: Al\(_2\)O\(_3\)/n-Si heterojunctions deposited at Ts equal to RT at various doping percentage of Co and Al\(_2\)O\(_3\) in the ZnO thin film are shown in figure (5) and (6) respectively. In general, the I-V curves of these heterojunctions under the forward bias and reverse bias voltage condition 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 and reverse current (I\(_f\)) 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 [27]. Also it can be seen from these figures that for both ZnO:Co /n-Si and ZnO: Al\(_2\)O\(_3\)/n-Si heterojunctions deposited at RT, the forward and reverse current increases with increasing doping percentage (1-5 wt.%) of Co and Al\(_2\)O\(_3\) 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.

Another noticeable remark from figure (5) and (6) that, in general, If were found to increase for ZnO:Co /n-Si and ZnO: Al\(_2\)O\(_3\)/n-Si heterojunctions deposited at RT upon doping ZnO thin film for pure ZnO and 5wt.% for both types of doping (Co and Al\(_2\)O\(_3\)) respectively. Exception to this behavior was found in the case of 0wt.% for Co-doped ZnO/n-Si and for 5wt.% Al\(_2\)O\(_3\)-doped ZnO/n-Si heterojunctions deposited at RT, within the range of voltage (0.0-1.0) V.

In general, from the inset of figure (5) and (6) it can be observed that I for ZnO:Co/n-Si and ZnO: Al\(_2\)O\(_3\)/n-Si heterojunctions deposited at RT and doped with Al\(_2\)O\(_3\) in the ZnO thin film is higher than that for ZnO:Co. Also it can be noted that I decreases with increasing doping Co concentration for of ZnO:Co /n-Si heterojunctions, whereas it increases with increasing doping Al\(_2\)O\(_3\) concentration for ZnO: Al\(_2\)O\(_3\)/n-Si heterojunctions within the range of voltage (0.0-1.0) V.

**Figure 5** Dark I-V characteristics in forward and reverse bias voltage for undoped and doped ZnO:Co/n-Si heterojunction at doping percentage of Co and deposited at at room temperature

**Figure 6** Dark I-V characteristics in forward and reverse bias voltage for undoped and doped ZnO: Al\(_2\)O\(_3\)/n-Si heterojunction at doping percentage of Al\(_2\)O\(_3\) and deposited at at room temperature
A semilogarithmic plots of the forward dark current versus applied voltage for undoped and doped ZnO:Co/n-Si and ZnO: Al₂O₃/n-Si heterojunctions deposited at RT are shown in figure (7) and (8) respectively. These plots can be classified into one region corresponding to the applied voltage, which is in agreement with Niraula et al [28] for ZnO:Co and ZnO: Al₂O₃/n-Si heterojunction. Also these figures show that in general, the reverse saturation current increases with the increasing doping percentage to 5wt.% for both Co and Al₂O₃ in the ZnO thin film. From the region, the ideality factor (β) has been calculated using equation.

\[
\beta = \frac{q}{kT} \frac{dV_f}{d[ln(I_f/I_s)]}
\]

Where the saturation current and it can be obtained by extrapolating the forward current curves to zero voltage. Table (3) listed the values of β for ZnO:Co and ZnO: Al₂O₃/n-Si heterojunctions respectively at different doping percentage for both Co and Al₂O₃ in the ZnO thin film which deposited at RT. The result in Table (3) shows that the value of β for undoped ZnO/n-Si heterojunction about 1.78 upon RT.

Table 3: Ideality factor values which obtained from I-V characteristics for undoped and doped ZnO:Co and ZnO: Al₂O₃ /n-Si heterojunction under Dark.

<table>
<thead>
<tr>
<th>Type of doping in ZnO</th>
<th>Ideality Factor (β)</th>
<th>Type of heterojunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>1.78</td>
<td>n</td>
</tr>
<tr>
<td>Co (1%)</td>
<td>1.84</td>
<td>n</td>
</tr>
<tr>
<td>Co (3%)</td>
<td>1.92</td>
<td>n</td>
</tr>
<tr>
<td>Co (5%)</td>
<td>2.58</td>
<td>n</td>
</tr>
<tr>
<td>Al₂O₃ (1%)</td>
<td>1.94</td>
<td>n</td>
</tr>
<tr>
<td>Al₂O₃ (3%)</td>
<td>1.75</td>
<td>n</td>
</tr>
<tr>
<td>Al₂O₃ (5%)</td>
<td>1.47</td>
<td>n</td>
</tr>
</tbody>
</table>

Also β is found to increase for ZnO:Co/n-Si heterojunctions deposited at RT upon increasing doping with Co up to 5wt.%, comparison with undoped thin films, while the value of β decreased with increasing doping percentage of Al₂O₃. In general, from Table (3) it can be observed that β value for Co-doped ZnO/n-Si heterojunctions deposited at RT is higher than that for Al₂O₃-doped.

![Figure 7: Semilogarithmic plot of forward bias of dark I-V curves for undoped and doped ZnO:Co/n-Si heterojunction at doping percentage of Co and deposited at at room temperature](image1)

![Figure 8: Semilogarithmic plot of forward bias of dark I-V curves for undoped and doped ZnO:Al₂O₃/n-Si heterojunction at doping percentage of Al₂O₃ and deposited at at room temperature](image2)
4.1 I-V CHARACTERISTICS for THE NANOSTRUCTURE UNDOPED AND Co, Al2O3 DOPED ZnO FILMS HETEROJUNCTION IN THE ILLUMINATED

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. The I-V characteristics at the forward and reverse-bias voltage in dark and under illumination from the ZnO side, with power meter for to Photo=2mw and Dark=4.4 µw for undoped and doped ZnO:Co/n-Si and ZnO: Al2O3/n-Si heterojunctions with various doping percentage of Co and Al2O3 deposited at RT are investigated. 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 (9) and (10) for ZnO:Co /n-Si and ZnO:Al2O3/n-Si respectively. It is observed that, in general, as mentioned previously the forward and reverse I-V characteristics in dark of these heterojunctions show an exponential behavior. Upon illumination of the junction, more carriers are generated and forward and reverse current increases. 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 [29].

The generated electron-hole pairs within the depletion width, and within a diffusion length outside of the depletion width are quickly swept away due to the strong electric field producing the photocurrent in the reverse-bias direction which increases with increasing of the incident light intensity due to the increase in the number of photo generated electrons and holes in the depletion region [29].

The outcome of above measurements indicates clearly a good response of these heterojunctions to illumination which makes it a candidate material for fabrication optoelectronic devices.

A semilogarithmic plots of the forward illumination current versus applied voltage for undoped and doped ZnO:Co /n-Si and ZnO:Al2O3/n-Si heterojunctions deposited at RT are shown in figure (11) and (12) respectively. Also it can be found from these Table (4) is that β for undoped and ZnO:Co/n-Si is higher than that for ZnO:Al2O3/n-Si heterojunctions deposited at RT. The ideality factor greater than unity can be attributed to the recombination of electrons and holes in the depletion region as well as the tunneling effect depending on the doping percentage on both sides of the heterojunction.
and on the presence of defect states [30]-[31]. Tunneling of carriers into states at the junction interface and subsequent recombination appears to be an important route of transport in ZnO/n-Si heterojunction.

**Table 4.** Ideality factor values which obtained from I-V characteristics for undoped and doped ZnO:Co and ZnO:Al$_2$O$_3$/n-Si heterojunction under illumination.

<table>
<thead>
<tr>
<th>Type of doping in ZnO</th>
<th>Ideality Factor (β)</th>
<th>Type of heterojunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>1.71</td>
<td>n</td>
</tr>
<tr>
<td>Co (1%)</td>
<td>1.78</td>
<td>n</td>
</tr>
<tr>
<td>Co (3%)</td>
<td>1.91</td>
<td>n</td>
</tr>
<tr>
<td>Co (5%)</td>
<td>2.29</td>
<td>n</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (1%)</td>
<td>1.64</td>
<td>n</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (3%)</td>
<td>1.37</td>
<td>n</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (5%)</td>
<td>1.18</td>
<td>n</td>
</tr>
</tbody>
</table>

**Figure 11** Semilogarithmic plot of forward bias of illumination I-V curves for undoped and doped ZnO:Co/n-Si heterojunction at doping percentage of Co and deposited at room temperature.

**Figure 12** Semilogarithmic plot of forward bias of illumination I-V curves for undoped and doped ZnO: Al$_2$O$_3$/n-Si heterojunction at doping percentage of Al$_2$O$_3$ and deposited at room temperature.

5. **SPECTRAL MEASUREMENTS FOR ZnO:Co, Al$_2$O$_3$/n-Si HETEROJUNCTION**

Spectral photoresponse measurements were done in the 300–1200 nm range, using a xenon lamp light source, a single-pass monochromator and a calibrated n/Si photodetector. Figures (13) and (14), shows the measured spectral quantum efficiency of a ZnO:Co and ZnO:Al$_2$O$_3$/n-Si UV detector under reverse bias voltages ranging about 4V. The quantum efficiency increased with increasing doping Co at 3wt.%, comparison with undoped thin films, while the value of quantum efficiency decreased with increasing doping percentage of Al$_2$O$_3$, whereas it increases with undoped ZnO/n-Si and reached a maximum value of ~137% at 284nm for ZnO:Co/n-Si and ~99% at 293nm for ZnO:Al$_2$O$_3$/n-Si under 4 V reverse bias. The cutoff wavelength red shifted with doping for both ZnO:Co/n-Si and ZnO:Al$_2$O$_3$/n-Si, from 283 to 400 nm and 290 to 420 nm for 4 V reverse bias, respectively. Since $\lambda_c<500$nm was satisfied, true solar-blind detection was successfully demonstrated.
The corresponding device responsivity curve under 4 V reverse bias is shown in Figures (13) and (14). A peak responsivity of 0.33 A/W at 320 nm for ZnO:Co/n-Si and 0.25 A/W at 340 nm for ZnO:Al₂O₃/n-Si is measured. The responsivity drops sharply around 339 nm ZnO:Co/n-Si and 360 nm for ZnO:Al₂O₃/n-Si and a solar-blind/near-UV contrast of 4 orders of magnitude is observed within 80 nm.

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

$$D^* = R_\lambda \frac{R_0 A}{4KT}$$  

Where $R_\lambda$ 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 $1.1x10^{13}$ cm Hz$^{1/2}$/W, which corresponds to a setup limited Noise Equivalent Power (NEP) of $18.54x10^{-13}$ W/Hz$^{1/2}$ and of $17.6x10^{-13}$ cm Hz$^{1/2}$/W, which corresponds to a setup limited NEP of $13.09x10^{-13}$ W/Hz$^{1/2}$ for ZnO:Co/n-Si and ZnO:Al₂O₃/n-Si, respectively.

Finally, noise characterization of the solar-blind Schottky detectors were carried out in the frequency range of 1 Hz – 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 1 V, the detector noise did not exceed the measurement setup noise floor of $3x10^{-29}$ A$^2$/Hz around 10 kHz. Therefore, we have measured devices with higher leakage currents in order to observe the bias dependence of the spectral noise density[32].
6. CONCLUSIONS

Studies of ZnO nanostructure thin films and ZnO/n-Si heterojunctions were performed in an attempt to enhance understanding how processing steps including the addition of Co and Al$_2$O$_3$ in ZnO thin film affects the film's and heterojunction's properties. From the results of these studies it can be concluded that:

1. The films deposited from pure ZnO, 3 wt.% Co and 5 wt.% Al$_2$O$_3$ doped ZnO targets at oxygen pressure of ($10^{-4}$) mbar, (460°C) substrate temperature and laser fluency (1.6) J/cm$^2$ are good candidates for structural, morphological, electrical characterization and spectral responsivity.

2. The XRD studies indicate that the deposited ZnO thin films on n-Si substrate are polycrystalline and grown of the hexagonal phases, and the preferred orientations are (111) for the silicon and (100) for the ZnO and ZnO:Co,Al$_2$O$_3$ films.

3. Grain size for (100) plane increasing doped in ZnO thin films. It was found also in morphological properties (SEM). The film deposited at an optimum cobalt and alumina concentration 5wt.% exhibited more intensity maintaining average RMS roughness of 55.78nm and 67.88nm respectively.

4. I-V characteristics in dark and under illumination for ZnO:Co/n-Si nanoparticles show that the ideality factor β for undoped ZnO is 1.95 at under dark and 1.4 at under illumination, and increase for 1wt.% rate and decreases in 3 wt.% and 5 wt.% upon increase with Co percentage, while decreases with Co, while decreases with Al$_2$O$_3$ concentration. I-V characteristics under illumination for ZnO:Co and ZnO:Al$_2$O$_3$/n-Si nanoparticles, indicate clearly a good response to illumination which make it a candidate material for fabricating optoelectronic devices.

5. Demonstrated solar-blind based Schottky photodiodes with low dark current, low noise, and high detectivity. Breakdown voltages larger than 4 V reverse bias were achieved. Device responsivities as high as 0.33A/W at 320 nm for ZnO:Co/n-Si and 0.25 A/W at 340 nm for ZnO:Al$_2$O$_3$/n-Si were measured under 4 V reverse bias. Detector noise was 1/f limited with spectral noise density values less than of 13.09x10$^{-13}$ W/Hz$^{1/2}$ for ZnO:Al$_2$O$_3$/n-Si under reverse bias voltages as high as 1V.

6. The spectral response parameters results ensure the construction of high quality detectors, and the shape spectrum of nano ZnO:Co, Al$_2$O$_3$/n-Si extends to the blue region, due to widening the window band gap.

References


