The Improvement Photoresponsivity of ZnO Based Photodiode with Indium Doping

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Abstract: The heterojunction photodiodes with undoped ZnO and Indium (In) doping ZnO thin films have been grown on p type silicon wafer by solution based spin coating method. The crystal structure analyzes of the films show that they have amorphous nature. The electrical characterizations of diodes have been performed by classical I-V and C-G-V technique. The minimum ideality factor of 3.97 and minimum series resistance of 7.2 kΩ have been recorded from 5% In doping ZnO/p-Si diode. The phototransient measurements show that photodiodes react fast to visible light and have a good reproducibility switching cycle. Similarly, the highest photosensitivity of 3.15×10³ and responsivity of 2.02 A/W have been obtained from 5% In doping ZnO/p-Si photodiode. This study indicates that the doping of In improves the electrical and optoelectrical performance of ZnO based photodiodes.

Keywords
Sol-gel, Photodiode, Indium, ZnO

1. Introduction

Transparent conductive oxides (TCOs) have recently been intensively studied in microelectronic and optoelectronic applications owing to their high electrical conductivity and high optical transparency [1-3]. TCO layers in optoelectronic devices are generally employed as collector and transporter of photogenerated electrons. Therefore, their optical transparency and electrical conductivity must be high [4]. Among the application of TCOs, the optoelectronic photodiode devices sense the incident light and convert it into electrical signals. When photons with higher energy than the optical band gap of photodiode device materials are absorbed, electron and hole pairs occur. These carriers create an increase in current and flow in an external circuit.

The photodiodes operate in reverse bias region. Therefore, the difference between the dark current and the photocurrent of photodiodes is clear in the reverse bias region compared with the forward bias region. The scientists carry out intensive studies on the improvement of the materials used in photodiode fabrication to enhance the light-sensing features of photodiodes. The photodiodes are utilized in various electronic and optoelectronic applications such as civil and military technology [5]. Among TCOs, ZnO is an attractive multifunctional material due to excellent properties such as low resistance, large exciton binding energy (60 meV), high direct broadband energy, high transparency, high thermal and mechanical stability [2,6,7]. Besides all these advantages, ZnO is non-toxic, environmentally friendly and economical due to its abundance in nature.

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The presence of intrinsic defects causes the ZnO to exhibit n-type electrical characteristics [8]. Also, the type and carrier concentration of ZnO can be altered with different dopant ions. Therefore, to enhance optical and electrical features of ZnO, doping is generally intended to replace the Zn$^{2+}$ ion with the dopant metal of higher valence electrons such as Indium (In$^{3+}$), Aluminum (Al$^{3+}$), Tin (Sn$^{4+}$) [2,9]. Suitable electronegativity and ionic radius, high oxidation resistance and low reactivity of In make it a more attractive dopant to improve photoelectrical performance of ZnO [10]. Also, it has been shown in many studies in the literature that In increases conductivity by increasing the carrier concentration of ZnO [8,11]. The high conductivity and transmittance obtained by In doping in ZnO thin films make it possible to fabricate high-speed photodetectors and transparent electrodes for solar cells [12]. The effect of In doping on the electrical and optical characteristics of the ZnO semiconductor film has been extensively studied. But, the effect of In doping on ZnO-based photodiodes has not been widely investigated. Therefore, there is still some lack of information to understand the behavior of low In doping on the optoelectronic parameters of the ZnO-based photodiode.

The ZnO thin films with In doping can be grown by various deposition methods such as rf helicon magnetron sputtering [12], pulsed laser deposition [13], remote-plasma-enhanced metalorganic chemical deposition (RPE-MOCVD) [14], electrospinning technique [15], sol-gel method [16]. Among these methods, the solution based spin coating has many advantages such as having low fabrication cost, no need for high vacuum, applicability method for large area deposition and suitability for laboratory experiments [17].

In this study, In was selected as dopant material for ZnO semiconductor material owing to the aforementioned advantages. The ZnO thin films with various indium concentrations were deposited on p-type Si to fabricate heterojunction structures. The aim of this study is to examine the influence of In doping on morphological and structural features of ZnO thin films and on the optoelectronic properties of fabricated diodes.

2. Materials and Methods

In this experiment, amorphous undoped ZnO and doped ZnO with various In percentage were coated on p-Si by spin coating method. The details of the experiment were given in our previous study [18]. Unlike the materials used in the previous experiment, only the Indium chloride (InCl$_3$) was used instead of the Tin (IV) chloride as a dopant source. Prepared undoped ZnO and doped ZnO solutions having different percentages of In were grown on the p-Si substrate with spin speed of 3000 rpm for 30s. The undoped and In doped ZnO films were subjected to preliminary drying at 300° C for 10 minutes. This process was repeated four times for each photodiode to ensure ZnO well deposited. After spin-coating and drying, all photodiodes were annealed at 750° C for 2h. Finally, aluminum was evaporated on top of ZnO thin films to form ohmic contact. Figure 1 illustrates the schematic structure of the photodiode. The crystalline structures of undoped and doped thin films, the surface roughness of thin films and optoelectrical properties of photodiodes were analyzed by X-ray diffractometer (XRD), Atomic Force Microscop (AFM) and Electrical Characterization System, respectively.

![Figure 1](image1.png)

Figure 1. The schematic diagram of the photodiode structure

3. Results

The crystallinity of thin films was performed by X-ray diffractometer (XRD) between 30° and 50°. The XRD pattern of thin films is indicated in Figure 2. All films indicate amorphous characteristics due to the absence of any sharp peak.

![Figure 2](image2.png)

Figure 2. The X-ray diffraction patterns of ZnO and In doped ZnO thin films

The surface roughness of thin films was indicated in Figure 3(a-e). The 3D AFM images of thin films illustrate that the morphologies of films are clearly influenced by In concentration. AFM images show that the films grow homogeneously without void and porosity. The values of the root mean square (RMS) roughness were obtained for undoped ZnO, 1%, 3%, 5% and 10% In doped films as 15.74 nm 13.24 nm...
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The increase in the roughness of the films with doping can be ascribed to the deposition of Indium oxide nanoparticles on the surface of the ZnO films [19]. Increasing the surface roughness of the films with the doping may cause an increase in the optical absorption of the films. The increase in optical absorption increases the number of photo-generated carriers. Thus, the responsivity of the photodiodes may be increased with In doping [7].

The I-V measurements of the photodiodes are illustrated under the dark condition and various irradiance intensities in Figure 4(a-e). The forward-to-reverse current ratio of photodiodes at ±4V varies between 1.86×10^3 and 4.23×10^3. Also, the electrical parameters of each photodiode are summarized in Table 1. When Figure 4 is examined, it is seen that the I-V characteristics of the photodiodes are directly related to the In doping concentration. To examine the electrical performance of diodes, the key electrical parameters of diodes can be obtained from Current-Voltage graphs by using standard heterojunction diode equation. The current of diode according to standard equation can be given as [20]:

\[ I = I_0 \left[ e^{\left(\frac{q(V - IR_s)}{n k T}\right)} - 1 \right] \]  

Here, \( I_0 \) is the saturation of reverse current, \( q \) is the electronic charge, \( n \) is the ideality factor, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( V \) is the voltage and \( R_s \) is the series resistance. The saturation current can be extracted from the extrapolation of linear part of forward I-V region. The \( \eta \) value which describes the diode performance can be extracted from the following equation:

\[ \eta = \left( \frac{q}{kT} \right) \left( \frac{\partial V}{\partial \ln(I/I_0)} \right) \]

When the obtained results are examined, the \( \eta \) values of diodes range from 3.97 to 5.67 for the varying In doping concentration. The \( \Phi_B \) values of diodes show increasing tendency from 0% to 1% In doping. Then, it decreases from from 3% to 10%. The trivalent In can increase the carrier concentration of ZnO because it acts as a donor in ZnO semiconductor layer [8,11]. Therefore, the decrease in barrier height in Schottky diodes can be defined by an increase in the carrier concentration depending on In concentration [21]. The ideality factor value is higher than 1, indicating that diodes exhibit non-ideal behavior.

\[ \Phi_B = \frac{kT}{q} \ln \left( \frac{I_d}{I_0} \right) \]

Figure 3. The 3D AFM images of ZnO and In doped ZnO thin films.
The non-ideal behavior of diodes is attributed to the interface layer, image force effects, series resistance and oxide layer between n-ZnO and p-Si [22]. The ideality factor and rectification ratio values of the fabricated photodiodes as well as the barrier heights ($\Phi_B$) values are summarized in Table 1. The reverse bias currents of the fabricated photodiodes increase with the light intensity, which is a typical characteristic of photodiodes. The internal and external electric fields are in the same direction in reverse bias for the depletion region of diodes. The recombination process in the reverse bias region takes place less than the forward bias. Therefore, the difference between dark and photocurrent is more clear in the reverse bias region [23]. This case shows that diodes exhibit photoconductivity behavior [24].

The photosensitivity is a key parameter for photodiodes and can be extracted from the following equation;

$$S = \frac{I_{\text{photocurrent}} - I_{\text{darkcurrent}}}{I_{\text{darkcurrent}}}$$

The highest photosensitivity value of photodiodes was obtained from 5% In doped ZnO/p-Si as $3.15 \times 10^3$ under 100 mW/cm² at -4V and tabulated in Table 1. When $\eta$ is higher than unity, it can be used the Norde [25] method to calculate some parameters of diodes such as series resistance and $\Phi_B$. This modified method can be expressed by the following equation;
behavior under a constant voltage [26,27]. Figure 6 indicates the transient photocurrent graphs of fabricated photodiodes. The transient photocurrent curves show exponentially increasing and decreasing photocurrents of photodiodes by switching the light on and off under various light intensities. The fast response of photodiodes to light and their reproducible switching cycle allows them to be a good candidate for photodetectors. Figure 7 (a) shows the responsivity (R) of photodiode versus In doping concentration. The R can be given by the following equation [28]:

\[
R = \frac{I_{\text{photocurrent}}}{I_{\text{inc}}}
\]  

Here, \( I_{\text{inc}} \) represent incident illumination power. The responsivity of photodiodes varies with In concentration. The \( R \)-values of the photodiodes increase by up to 5% In doping ZnO/p-Si diode, then decrease under 100mW/cm\(^2\) at -4V. The highest responsivity of 2.02 (A/W) was obtained from 5% In doping ZnO/p-Si diode. This high photoresponse value indicates that the sensitivity of ZnO can be improved by adequate In doping. The photoresponse values of the fabricated photodiodes are much higher than most published researches on the undoped and doped ZnO/p-Si photodiodes [26,29–31]. Also, to determine the photocconductivity mechanisms of photodiodes, the following equation can be used [32]:

\[
I_{\text{ph}} = A P^\beta
\]

Where \( I_{\text{ph}} \), A, P and \( \beta \) represent photocurrent, constant, light intensity and an exponent, respectively. The logarithmic graph of the light intensity versus the photocurrent was plotted and illustrated in Figure 7 (b). The values of \( \beta \) for photodiodes were extracted from the slope of Figure 7 (b) and tabulated in Table 1.

The \( \beta = 1 \) indicates that monomolecular recombination is dominant in the photodiode, \( \beta = 0.5 \) shows that bimolecular recombination is dominant. Whereas, 0.5 < \( \beta < 1 \) and 1 < \( \beta \) represent the presence of a continuous distribution of trapping centers in the band and photoconductivity mechanism with superlinear behavior, respectively [32,33].

### Table 1. The calculated electrical and optoelectrical parameters of photodiodes

| Diodes          | RR (dark,±4V) | n (1-V) | \( \Phi_b \) (1-V) (eV) | \( \Phi_h \) Norde (eV) | \( R_s \) Norde (kΩ) | \( \beta \) | S (4V,1-V) | Responsivity (A/W) |
|-----------------|---------------|---------|-------------------------|------------------------|----------------------|----------|-------------|-------------------|
| ZnO/p-Si        | 4.23×10\(^3\) | 4.72    | 0.71                    | 0.49                   | 43.9                 | 1.66     | 6.50×10\(^2\) | 0.30              |
| 1% In doped     | 9.62×10\(^2\) | 4.10    | 0.75                    | 0.54                   | 116.2                | 1.41     | 9.54×10\(^2\) | 0.57              |
| 3% In doped     | 8.65×10\(^1\) | 5.21    | 0.73                    | 0.51                   | 233.3                | 1.09     | 2.07×10\(^3\) | 0.95              |
| 5% In doped     | 1.86×10\(^1\) | 3.97    | 0.72                    | 0.50                   | 7.2                  | 1.13     | 3.15×10\(^3\) | 2.02              |
| 10% In doped    | 1.97×10\(^2\) | 5.67    | 0.67                    | 0.44                   | 14.4                 | 0.71     | 5.62×10\(^2\) | 1.67              |
Figure 6. The transient photocurrent graphs of photodiodes.

Figure 7. (a) The Responsivity versus In doping concentration of photodiodes (b) The logarithmic graph of the light intensity versus the photocurrent of photodiodes.
The \( C-V \) characteristics of fabricated photodiodes as a function of \( \text{In} \) doping is indicated in Figure 8 between 10 kHz and 1 MHz. The capacitance values of the diodes decrease with increasing frequency. This case is ascribed to the fact that the interface states of the diodes cannot follow the ac signal in the high frequency [34]. It is also seen from Figure 8 that diodes have negative capacitance values at 1 MHz frequency except for 3\% \( \text{In} \) doping \( \text{ZnO}/p-\text{Si} \) diode.

The negative capacitance is ascribed to the injection of minority carriers to polarization [7]. Figure 9 indicates the \( G-V \) characteristics of photodiodes between 10 kHz and 1 MHz. The conductance values of the diodes increase with increasing frequency. The conductance of the photodiodes reaches a maximum at certain voltages in the forward bias region and remains almost stable.
In summary, the undoped and In doping ZnO based photodiodes were fabricated by sol-gel spin coating methods. The structural and morphological of thin films were investigated by XRD and AFM, respectively. All films showed an amorphous structure nature with homogeneously grown on p-Si. The optoelectrical features of photodiodes were investigated by conventional I-V and C-G-V technique. The minimum ideality factor (3.97) and series resistance (7.2 kΩ) were obtained from 5% In doping ZnO/p-Si device. Also, the optoelectrical properties of photodiodes such as photosensitivity, photoresponsivity, and photoconductivity mechanism were studied under various visible illumination intensities. Similarly, the highest photosensitivity ($3.15 \times 10^3$) and responsivity (2.02

**Figure 9.** The $G$-$V$ measurements of photodiodes
A/W) were obtained from 5% In doping ZnO/p-Si photodiode. When all the obtained results are examined, it is shown that In doping can improve the properties of ZnO based photodiode and the fabricated heterojunctions can be used as a photosensor.

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