Research Article

Structural, Optical, Electrical, and Photoresponse Properties of Postannealed Sn-Doped ZnO Nanorods

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Tin (Sn) doped ZnO nanorods were synthesized on glass substrate using a sol-gel method. The synthesized nanorods were postannealed at 150, 350, and 500°C. The surface morphologies of Sn-doped ZnO nanorods at different postannealing temperatures were studied using scanning electron microscope (SEM). XRD results show that as the postannealing temperature increased from 150°C to 500°C, the c-axis orientation becomes stronger. Refractive indices and dielectric constants were calculated on the basis of different relationships by utilizing bandgap values. These bandgap values were obtained in terms of optical absorption by using a UV-Visible spectrophotometer. The enhancing effects of annealing temperatures on electrical properties were observed in terms of current-to-voltage measurements. Resistivity decreases as postannealing temperature increases from 150°C to 500°C. Annealed samples were evaluated for UV-sensing application. The samples exhibit a responsivity of 1.7 A/W.

1. Introduction

Zinc oxide is an n-type semiconductor with bandgap energy of 3.37 eV and large exciton binding energy of ~60 meV. ZnO and its alloys are having vast device applications such as light emitting diodes (LEDs), solar cells, and optical waveguides [1–3]. ZnO is nontoxic, highly transparent along with high mechanical and thermal stability. Several researchers explore that the dopants can improve the electrical and optical properties of ZnO such as Al, In, and Sn [4–6]. When Sn was added into ZnO for doping, Sn$^{4+}$ substitutes Zn$^{2+}$ site in the ZnO crystal structure resulting in two more free electrons to contribute to the electric conduction [7]. The ionic radius of Sn$^{4+}$ (0.069 nm) is smaller than Zn$^{2+}$ (0.074 nm); therefore, Sn$^{4+}$ ions can replace Zn$^{2+}$ ions in substitution sites [8].

ZnO can be prepared by varieties of different techniques such as pulsed laser deposition (PLD) [9], RF sputtering [10], chemical vapor deposition (CVD) [11], sol-gel [12], metal organic chemical vapor deposition (MOCVD) [13], and molecular beam epitaxy (MBE) [14]. Among them, sol-gel is the mostly used technique for ZnO preparation; it is low cost, needs low temperature, and can be implemented for large-scale preparation as compared to other techniques [15].

In the present study, Sn-doped ZnO nanorods were successfully synthesized using sol-gel method. We also investigated the effects of postannealing temperatures on structural, optical, electrical, and photoresponse properties. The results of this investigation contribute to the application of synthesized nanostructures in optical devices and heterojunction solar cells.

2. Experimental

ZnO seed solution was prepared by using low cost sol-gel spin coating method as reported in our previous research [16]. Briefly, 3.84 g zinc acetate dihydrate was dissolved in 50 mL 2-methoxyethanol and 1.069 g monoethanolamine. Monoethanolamine acts as a stabilizer and was added drop-wise under stirring and constant temperature. Thus, a ZnO solution of concentration 0.35 M was prepared. The solution was stirred for 2 hours at 60°C until a transparent and homogeneous solution was obtained. The prepared solution was stored overnight at room temperature. The aged solution was spin-coated on glass substrate using spin coater which was rotated at 3000 rpm for 30 s. The film was heated at 250°C
for 20 min after each coating. The coating-to-drying process was repeated for five times, and thus produced films were annealed at 500°C for 1 hour.

The ZnO nanorods were grown on seeded glass substrate using hydrothermal growth method. The growth solution was prepared by mixing zinc nitrate hexahydrate (0.1 M), tin chloride dihydrate (0.001 M) and hexamethyldiamine (0.1 M) in 150 mL deionized water (DI). The solution was sonicated for 30 min at 50°C in an ultrasonicator (Delta DC200H). The seeded substrates were placed vertically so that the seeded side was facing down in the growth solution. The growth was done in a preheated oven at 93°C for 6 hours. After the growth, samples were washed with DI water to remove the residual salts and dried using N2 gun. The synthesized samples were postannealed at temperatures of 150, 350, and 500°C for 1 hour under ambient environment. Silver electrodes were deposited on the top of Sn-doped ZnO nanorods using hard mask. The metal was evaporated via Edwards Auto 306 thermal evaporation in a vacuum environment.

The surface morphology of Sn-doped ZnO nanorods was examined using scanning electron microscopy (SEM JEOLE6460LA). The crystal structure and orientation of Sn-doped ZnO nanorods were investigated using X-ray diffractometer (XRD, Bruker AXS D8 Advance). The UV-Visible (UV-Vis) spectra of Sn-doped ZnO nanorods were obtained using a Lambda35 UV-Vis spectrometer (Perkin Elmer). A Keithley 2400 source meter was used to determine current-to-voltage (I-V) and current-to-time (I-t) characterization. Optical properties were determined by UV-Vis spectroscopy (HP 8453, Agilent). A digital lock-in amplifier (SR 830) and a 500 W Xenon lamp (SVX 1450) were used to characterize the spectral response. All of the measurements were performed in an ambient environment.

3. Results and Discussion

Figure 1 depicts the XRD pattern of Sn-doped ZnO nanorods postannealed at temperatures of 150, 350, and 500°C. The obtained spectra showed several peaks at (002), (101), (102), (103), and (004) planes, which are consistent with previously reported values [17–21]. All the diffraction peaks are associated with the JCPDS card no. 036-1451 of the hexagonal ZnO structure.

No other peaks of impurities such as zinc nitrate hexahydrate and hexamethyldiamine were observed in the spectra. It was observed that all the postannealed Sn-doped ZnO nanorods have preferential growth at (002) orientation. The intensity of peak appeared at (002) plane found increased with an increase in postannealing temperature. The intensification of peak that appeared at (002) plane indicates that crystal quality of the synthesized Sn-doped ZnO nanorods gets improved with the increase in postannealing temperature. The average crystalline size was calculated using Scherrer's formula [22–24]:

\[
D = \frac{0.9\lambda}{B \cos \theta},
\]

where \(D\) is the crystalline size, \(\lambda\) is the wavelength of X-ray, \(\theta\) is the angle of diffraction, and \(B\) is the FWHM of the observed peak. The calculated crystallite size values were 30, 32, and 36.9 nm with respect to postannealing temperatures of 150, 350, and 500°C, respectively, which revealed that crystallite size increased as the postannealing temperature increased. The increment in crystalline size may be attributed to particles merging activity at high postannealing temperature [25].

Figure 2 illustrates the SEM images of Sn-doped ZnO nanorods postannealed at temperatures of 150, 350, and 500°C, respectively. It was notified that all the substrates were densely covered with vertically aligned nanorods. As the postannealing temperature increased from 150 to 500°C, the Sn-doped ZnO nanorods showed noticeable variations on the surface morphology as shown in Figures 2(b) and 2(c). Based on dynamics growth and thermodynamics process, particles likely move more disorderly at maximum postannealing temperature than at other temperatures; as a result, the anisotropic growth of crystals is perturbed because of the surrounding driving force; hence, Sn-doped ZnO nanorods show a granular shape (Figures 2(b) and 2(c)) [26]. Furthermore, Sn-doped ZnO nanorods at a higher postannealing temperature are more agglomerated and spherical than those at a lower postannealing temperature; this result indicates that the samples are highly crystalline in nature [27].

The inset of Figure 3 shows the absorbance spectra, which displayed that as the postannealing temperature increases, the absorbance edge shifts towards the lower wavelength, indicating expansion in the optical bandgap. The optical bandgap of direct-transition semiconductor Sn-doped ZnO nanorods was calculated using Tauc model [28] and compared with the reported values [19, 20]:

\[
\alpha h\nu = A (h\nu - E_g)^{1/2},
\]

where \(\alpha\) is the absorbance coefficient, \(h\nu\) is the photon energy, \(A\) is an energy independent constant, and \(E_g\) is the energy gap. The optical bandgap of Sn-doped ZnO nanorods which
Figure 2: SEM images of Sn-doped ZnO nanorods at different postannealing temperatures (a) 150°C, (b) 300°C, and (c) 500°C.

were postannealed at temperatures of 150, 350, and 500°C was determined by extrapolating the straight section of the plot of \((\alpha h\nu)^2\) versus photon energy as shown in Figure 3.

The calculated values of the optical bandgap energy were 3.18 eV, 3.21 eV, and 3.33 eV for the samples postannealed at temperatures of 150, 350, and 500°C, respectively. The change in bandgap energy may be attributed to the electron-electron and electron impurity scattering [29, 30].

Our knowledge of refractive index \(n\) is important in the advancement of different materials in optoelectronic research. Therefore, \(n\) as a function of wavelength is an important parameter and should be evaluated for the design of various devices, such as integrated optical switches, filters, and modulators. Efforts have been devoted to relate \(n\) to energy gap \((E_g)\) based on simple relationships [31–35]. In the present study, various relationships between \(n\) and \(E_g\) were
Table 1: Energy gaps \( (E_g) \), calculated refractive indices \( (n) \) and optical dielectric constant \( (\varepsilon_{\infty}) \) of nanostructure Sn-ZnO using Ravindra et al. [35], Hervé and Vandamme [36], and Ghosh et al. [37] models.

<table>
<thead>
<tr>
<th>Annealing temperatures ( (^\circ C) )</th>
<th>Band gap energy ( (eV) )</th>
<th>Refractive index ( (n) )</th>
<th>Optical dielectric constant ( (\varepsilon_{\infty}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>3.18, 3.44(^b), 0.73(^c), 0.88(^d), 2.26(^e)</td>
<td>2.0764(^f), 2.2960(^h), 2.3335(^i), 2.008(^j)</td>
<td>4.3114(^k), 5.2716(^l), 5.4452(^m)</td>
</tr>
<tr>
<td>350</td>
<td>3.21</td>
<td>2.0578(^j), 2.2876(^h), 2.3274(^h)</td>
<td>4.2345(^l), 5.2331(^m), 5.4167(^n)</td>
</tr>
<tr>
<td>500</td>
<td>3.33</td>
<td>1.9834(^j), 2.2546(^h), 2.3037(^h)</td>
<td>3.9338(^k), 5.0832(^l), 5.3070(^n)</td>
</tr>
</tbody>
</table>

\(^a\)Huemmer [39]—Exp.
\(^b\)Charifi et al. [41]—Theor.
\(^c\)Schleife et al. [42]—Theor.
\(^d\)Xu and Ching [43]—Theor.
\(^e\)Schröer et al. [44]—Theor.
\(^f\)Hervé and Vandamme [36].
\(^g\)Ghosh et al. [37].
\(^h\)Ravindra et al. [35].

reviewed. Ravindra et al. [35] suggested that different relationships are present between bandgap and high-frequency \( n \), in which a linear form of \( n \) as a function of \( E_g \) is presented as follows:

\[
n = \alpha + \beta E_g, \tag{3}
\]

where \( \alpha = 4.048 \) and \( \beta = -0.62 \) eV\(^{-1}\). Light refraction and dispersion are also considered. Hervé and Vandamme [36] proposed an empirical relationship as follows:

\[
n = \sqrt{1 + \left( \frac{A}{E_g + B} \right)^2}, \tag{4}
\]

where \( A = 13.6 \) eV and \( B = 3.4 \) eV. Ghosh et al. [37] showed an empirical relationship for groups II to VI semiconductors on the basis of the band structure and quantum dielectric considerations of Penn [38] and Van Vechten:

\[
n^2 - 1 = \frac{A}{(E_g + B)^2}, \tag{5}
\]

where \( A = 25E_g + 212 \), \( B = 0.21E_g + 4.25 \), and \( (E_g + B) \) refer to an appropriate average optical energy gap of the material. The calculated \( n \) of the end-point compounds and \( E_g \) (Table 1) are consistent with experimental [39, 40] and theoretical [41–44] values. These results are verified by calculating the optical dielectric constant \( \varepsilon_{\infty} \), which is dependent on \( n \); hence, \( \varepsilon_{\infty} = n^2 \) [45]. The \( n \) obtained using the Hervé and Vandamme model [36] is important to enhance the detecting and sensing of ZnO nanostructure. Therefore, high absorption may be attributed to an increase in sensor efficiency.

Current-to-voltage characteristic was carried out to study the postannealing effect on the electrical properties of Sn-doped ZnO nanorods. The effect of postannealing temperature can be visually inspected in current-voltage characteristic curves of Figure 4.

The linear relationship between current-to-voltage curves demonstrates the ohmic nature of Sn-doped ZnO nanorods. The resistivity \( \rho \) at postannealing temperatures of 150, 350, and 500\(^\circ \)C can be calculated from the \( I-V \) curves by using the following relation:

\[
\rho = R \left( \frac{A}{T} \right), \tag{6}
\]

where \( R \) is the resistance, \( A \) is the area of electrodes, and \( l \) is the length of nanorods. Resistivity values of Sn-doped ZnO nanorods annealed at temperatures of 150, 350, and 500\(^\circ \)C were \( (316.75 \times 10^6) \), \( (55.89 \times 10^6) \), and \( (20.95 \times 10^6) \) \( \Omega \cdot \text{cm} \), respectively. It can be revealed that the decrement in electrical conductivity was a causative factor due to reduced grain-boundary scattering and an increase in electron mobility with grain size growth [46].

Our X-ray diffraction result is consistent with those in previous studies [47–51], in which crystallinity is improved with respect to annealing temperature. Photoresponse \( (I_{on}/ I_{off}) \) increases as annealing temperature increases [52–58]. In ZnO-type materials, photoresponse is generally caused by oxygen desorption and adsorption process originating from either a bulk- or surface-related process [52, 59, 60].

Figures 5(a) and 5(b) show the responsivity and photoresponse curves of the Sn-doped ZnO nanorods post-annealed at 150, 350, and 500\(^\circ \)C. In this study, the sharp cutoff in the responsivity curves decreased in magnitude at approximately 370 nm. The maximum responsivity of our sensor at an applied bias of 5 V was 1.7 A/W, which is higher than previously reported values [61, 62]. The photoresponse spectra also showed that UV light response occurs faster than previously reported values [61, 62]. The photoresponse also showed that UV light response occurs faster than previously reported values [61, 62].
Figure 3: A plot of \((\alpha h \nu)^2\) versus photon energy for Sn-doped ZnO nanorods at different postannealing temperatures.

Figure 4: \(I-V\) curves of Sn-doped ZnO nanorods postannealed at different temperatures.

axis [63, 64]. However, electrons experience resistance along the nanorod axis at low annealing temperatures; as a result, photoresponse is decreased.

4. Conclusion

Sn-doped ZnO nanorods were successfully synthesized on glass substrate by low temperature sol-gel method. The effect of postannealing temperature on the structural, optical, electrical, and photoresponse properties of Sn-doped ZnO nanorods is investigated using X-ray diffraction, UV-Vis spectroscopy, \(I-V\), and \(I-t\) measurements, respectively. The crystallinity and \(c\)-axis orientation of the Sn-doped ZnO nanorods were increased with annealing temperatures. The optical bandgap energy of Sn-doped ZnO nanorods decreased as the annealing temperature increases. Electrical characteristics reveal the effect of annealing temperature on the resistivity and photoresponse of Sn-doped ZnO nanorods. Hence, the proposed Hervé and Vandamme model and the improved photoresponse of postannealed samples are applicable in optoelectronic devices.

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