Photosensing effect of indium-doped ZnO thin films and its heterostructure with silicon

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ABSTRACT
Indium-doped zinc oxide (ZnO) thin films were coated onto glass and silicon substrates at different indium concentrations (0%, 2.5%, 5%, and 7%) using successive ionic layer adsorption and reaction (SILAR) method. Furthermore, crystalline structural, morphological, and elemental properties of indium-doped ZnO thin films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and EDAX techniques. Moreover, the optical properties were analyzed using UV–vis optical absorption, photoluminescence (PL), and Raman spectroscopy techniques. XRD analysis confirmed the growth of ZnO films with perfect inclusion of indium ions into the ZnO lattice of the hexagonal wurtzite structure. Moreover, the optical studies showed improved transmittance and band gap with the indium doping of up to 2.5%. The photosensor fabricated using the ZnO film doped with 2.5% indium concentration exhibited maximum response regarding sensing properties. A p–n heterojunction device fabricated by coating the 2.5% indium-doped ZnO on p-Si substrate showed good rectifying property with photovoltaic nature, and it responded well for UV region.

1. Introduction
Recently, semiconducting oxides have been explored much for several sensing applications, including photosensing. Zinc oxide (ZnO) is an exciting oxide semiconductor among various oxide materials, used for numerous applications due to its favorable electrical and optical properties [1–3]. Moreover, ZnO is a less toxic, low-cost material showing excellent optical and electrical properties. It has a wide band gap (3.32 eV).
and high exciton binding energy (~60 MeV) with n-type conductivity; therefore, it is used in numerous applications including light emitting diodes, UV and visible photodetectors, gas sensors, solar cell, and transparent conducting electrodes [4–7]. The high electron mobility of the ZnO reduces the recombination losses and increasing the efficiency of solar cells [8]. Its low-cost and nontoxic nature attracts wide attention for various nanoelectronic and sensor devices. Moreover, it can be synthesized into various morphologies, such as nanorods, nanoparticles, nanotubes, and nanoflowers, suitable for a specific application. Furthermore, doping of metallic ions with ZnO is expected to improve its electrical and optical properties to produce efficiency-enhanced electronic devices by increasing transparency, electrical conductivity, electron mobility, and porosity [9–12]. Various dopants such as Ga, Al, Sn, Mg, and In are used to dope ZnO to enhance its electrical and optical properties [5,13–22]. Indium (In) is a potential dopant for n-type ZnO because it is a highly stable and low resistive element [23]. Additionally, it has high valence with suitable electronegativity, low reactivity, and high oxidation resistance [24]. Moreover, it can also offer high transmittance and high conductivity favorable for optoelectronic applications.

 Recently, different techniques, such as sputtering, chemical vapor deposition, molecular beam deposition, electrodeposition, pulsed laser deposition, sol–gel spin coating, and chemical spray pyrolysis, have been used to grow In-doped ZnO. However, the reports on In-doped ZnO thin films coated using successive ionic layer adsorption and reaction (SILAR) process for photodetector applications are limited [25,26]. The SILAR method has several advantages compared to other methods for preparing oxide-based thin films [27,28]. It is a simple and cost-effective method suitable for producing uniform crystalline films on every conductive and no-conductive substrates with good adhesion using chemical solutions at room temperature; in this process, the substrate is immersed alternatively in cationic and anionic precursor solutions and rinsed with water between the immersions [29]. This paper presents the optical sensing property of the In-doped ZnO thin films coated onto glass and silicon substrates using the SILAR technique with different In concentrations. Moreover, we report on morphological, structural, electrical, and optical properties of In:ZnO thin films.

2. Experimental details

We used analytical grade chemicals to coat In-doped and undoped ZnO thin films on glass and p-type silicon substrates. Before coating, the substrates were cleaned using soap solution well, DI water, and acetone with ultrasonication; thereafter, they were dried with N₂ gas blowing. The undoped ZnO thin films were deposited by dipping the substrates alternately in sodium zincate (Na₂ZnO₂) solution and hot water baths maintained at room temperature and near boiling temperatures, respectively. For the growth of In-doped ZnO, indium chloride (InCl₃) was added with the sodium zincate bath. The cationic precursor – sodium zincate solution – for the deposition was prepared by adding 0.1 M zinc sulfate (ZnSO₄) and 1 M NaOH to grow undoped ZnO. Whereas, different concentrations of indium chloride (0, 2.5, 5, and 7.5 wt%) was added with the sodium zincate solution to grow In-doped ZnO. After cleaning and drying, the substrate was immersed first in a sodium zincate bath for 20 s and then transferred to hot water. This immersion process was continued 100 times to build the thickness of the film after drying the substrate at each cycle using a hot air jet. A thin layer of sodium zincate complex was produced when the substrate was dipped into the sodium zincate bath. The sodium zincate complex was then decomposed into ZnO while dipping it in a hot water bath.

The prepared films were annealed at 250°C for 30 min using a hot air oven after completing the coating process. The thickness of the films was calculated using a stylus profilometer. Furthermore, surface morphology and compositional properties of the grown films were measured using JEOL 6360 model scanning electron microscope (SEM) attached with EDAX setup. Moreover, the microstructural properties of the films were analyzed using X’pert Pro PANalytical X-ray diffractometer with CuKα radiation (λ = 1.5418 Å). Optical absorption studies of the films were conducted using a UV–vis spectrophotometer (Shimadzu-UV 1800) in the range of 300–900 nm. Photoluminescence study of the films was performed using a Thermo Fisher photoluminescence spectrometer at an excitation wavelength of 450 nm. The doping-dependent microstructural changes of the films were analyzed using Raman spectra obtained using laser excitation with the wavelength of 532 nm. Ag metal contacts were formed on the films coated on glass substrates for photosensing studies of the In-doped and undoped ZnO films. Photocurrent–voltage responses were recorded using a Keithley source meter (model 2450) employing an optical source of 532 nm wavelength. Furthermore, a 2.5% In-doped ZnO film was coated on a p-type silicon substrate. Its photosensing properties were studied using a source meter (Keithley Instruments 2611B; Cleveland, OH, USA) under different illumination conditions to analyze the heterostructural property of In-doped ZnO with silicon. Ag metal contacts formed on In:ZnO and silicon surfaces were used to measure the photocurrent variations that were produced in the In:ZnO/p-Si heterojunction.
3. Results and analysis

3.1. Morphological and compositional analysis

Field emission scanning electron microscopic (FE-SEM) technique was used to analyze the surface morphological variation of the ZnO thin films due to the change in In doping. The FE-SEM images of the In-doped ZnO films are shown in Figure 1. It shows indium doping concentration-dependent morphology of In:ZnO thin films. The In-doped ZnO thin films were composed of multi-shaped grains of various sizes covering the whole substrate uniformly without any cracks or pin-holes. Indium concentration of 2.5% produced grains of bigger sizes than other higher concentrations.

Figure 1 shows high aspect ratio rods and cone-shaped particles of varying sizes from 200 nm to 2 µm. Indium doping was found to increase the film thickness besides improving crystallite grains. Moreover, the 7.5% In-doped films showed evenly spread small and more uniform grains on the substrate. This infers that more number of nucleation centers were produced causing formation of large number of smaller size grains at higher doping concentration, it justifies the doping concentration-dependent morphological variation. The indium doping concentration of 2.5% was found to be an optimum doping concentration for crystalline improved morphological films.

To further analyze, particle size distribution histograms were obtained using Image-J software. Figure S1 (Supplementary materials) displays particle distribution histograms of the films prepared using different In concentrations. It indicates average particle size of 0.4 µm is increased to 0.8 µm for the increase of In concentration to 2.5 wt%. For further increase of In concentration from 2.5 wt%, the average particle size is reduced depending upon the In concentration, which indicates the influence of In concentration in formation of ZnO morphologies.

EDAX spectrum was obtained for different In-doped ZnO films to examine the elemental composition and to confirm the inclusion of indium in the prepared films. The EDAX images shown in Figure S2 confirms the inclusion of indium in the films depending upon the precursor indium concentrations. Table S1 shows elemental composition of In:ZnO thin films grown at different In concentrations. It shows increased doping concentration for the increase of precursor concentrations.

3.2. Structural analysis

Structural properties of the In-doped ZnO were studied using X-ray diffraction. The X-ray diffraction patterns of various concentrations of In-doped and undoped ZnO thin films are shown in Figure 2. All the peaks indicate the growth crystalline ZnO thin films of hexagonal wurtzite structure with predominant orientation along (002) plane (JCPDS File No. 36–1451) [1,30]. No extra peaks, other than ZnO, is observed even at higher doping concentration. Moreover, the absence of indium-based impurity and other phases indicate the phase purity of In-doped ZnO thin films grown using

![Figure 1. FE-SEM images of ZnO thin films prepared with various In concentrations: (a) 0%, (b) 2.5%, (c) 5.0%, and (d) 7.5%.](image-url)
the SILAR technique. All the doped and undoped films displayed peaks at (100), (002), (101), (102), (110), (103), and (201). The peak (002) is highly intense, indicating the highly oriented growth of crystallites of In:ZnO thin films along c-axis. However, the predominant peak intensity was changed based on the doping concentration, denoting the concentration-dependent microstructural changes. Figure 3 shows that the XRD peak (002) is shifted toward a higher angle when In concentration increases to 2.5%; after that, the angle reduces when concentration is increased further. The left-handed and right-handed shifts indicate the crystallite variation-dependent strain and lattice relaxations. The residual stress can shift the peak in one direction to balance the strain at the grain boundaries. Similarly, a relaxed strain can shift the peak in the opposite direction. The shift in XRD peak toward high angle with increased intensity is caused by relaxed strain, implying the improved crystallinity. This indicates the dopant concentration-dependent modification of lattice strain and other parameters [2,31]. The crystallite size of the films was estimated using the Debye-Scherer formula (Equation (1)). As shown in Table 1, the crystallite size increases as the In-doping concentration increases from 0% to 2.5%; however, it decreases as the concentration further increases from 2.5% to 7%. This decrease in crystal size at higher concentrations indicates the crystalline imperfection caused due to the higher doping, which indicates deterioration of crystalline quality due to excessive inclusion of dopant ions, as shown in the XRD peaks [32]. A similar phenomenon was reported by Benzitouni et al. [1]. This change in crystallite size and strain values may arise due to difference in ionic radii between Zn (Zn$^{2+}$ = 0.74) and In (In$^{3+}$ = 0.80). The excessive inclusion of In ions into the ZnO lattice can segregate in the grain boundaries causing microstructural modification, which means that crystallite size increases with increasing strain. This segregation of excess In ions into the grain boundaries impedes the lateral growth of grains, causing the formation of (002) oriented tiny crystallites and shifting the 2θ to smaller angles. Moreover, the crystallite size was calculated by the Debye–Scherer formula (Equation (1)) considering the prominent XRD peak (002) [33].

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)
where \( \lambda \) denotes the wavelength of X-ray, \( \beta \) represents full width at half maximum (FWHM), and \( \theta \) denotes the 2\( \theta \) angle of XRD peak (002). The crystalline defects produced in the films can be calculated from the changes in microstrain (\( \varepsilon \)), dislocation density (\( \delta \)), and quantity of crystallites (\( n_c \)). They were calculated using Equations (2), (3), and (4), respectively [33].

\[
\varepsilon = \frac{\beta \cot \theta}{4} \quad (2)
\]

\[
\delta = \frac{1}{D^2} \quad (3)
\]

\[
n_c = \frac{t}{D^3} \quad (4)
\]

where \( t \) denotes the thickness of the film. The different values of the parameters estimated are given in Table 1. The microstrain value decreased up to the optimum value of concentration (2.5%), and then it is increased, denoting the distorted lattice.

The lattice constants of the crystalline structure were determined using the Equations (5) and (6) [23].

\[
2d_{hkl}\sin\theta = n\lambda \quad (5)
\]

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + hk}{a^2} \right) + \frac{\beta^2}{c^2} \quad (6)
\]

where \( d_{hkl} \) represents the interplanar spacing and \( hkl \) denotes Miller indices, and \( n \) represents the order of diffraction; moreover, the constants \( a \) and \( c \) represents the lattice parameters of the hexagonal system. The calculated lattice parameters are also given in Table 1.

### Table 1. Indium concentration-dependent crystallite size, strain, lattice parameters, and cell volume of In:ZnO thin films.

| In doping level [%] | Film thickness [nm] | Crystallite size [nm] | Microstrain (\( \varepsilon \)) \( \times 10^{-3} \) | Doslocation density (\( \delta \)) \( \times 10^{13} \) [Lines/m\(^2\)] | Lattice parameters | Number of crystallites \( \times 10^{16} \) [m\(^{-2}\)] |
|-----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|
| 0.0             | 510             | 68.1            | 1.74           | 2.16           | 3.217 5.194 3.17 | |
| 2.5             | 560             | 69.3            | 1.67           | 2.08           | 3.235 5.189 3.00 | |
| 5.0             | 585             | 68.7            | 1.70           | 2.12           | 3.241 5.196 3.08 | |
| 7.5             | 600             | 67.5            | 1.73           | 2.19           | 3.247 5.208 3.25 | |

Figure 4. (a) Optical absorption, (b) optical transmittance, (c) Tauc plot (inset: Band gap variation), and (d) photoluminescence spectra of ZnO thin films of various In concentrations.
3.3. Optical characterization

The effect of indium doping on zinc oxide thin films prepared by the SILAR technique was also analyzed using optical absorbance. Figure 4 shows the UV–vis absorbance spectrum recorded in the 300–900 nm range for the ZnO films with different indium concentrations. It shows the highest absorption in the UV region compared to the visible region, indicating the property of ZnO. The 2.5% In-doped ZnO shows a little higher UV absorption than undoped and higher indium-doped ZnO thin films. Moreover, the split of UV absorption peak, as displayed in the inset of Figure 4(a), indicates the split of Zn\(^{+2}\) d electron energy level due to the crystal field effect. The strong absorption in the UV region can transfer the electrons to the conduction band from valence band, causing band gap extension and intermediate levels to absorb more light.

The optical transmittance of the films is displayed in Figure 4(b), which indicates that the films have high transparency after 400 nm depending on the concentration of the indium doping effect. The transparency increases with the increasing indium concentration. However, it decreases at higher doping concentrations. This decrease in transmittance due to the inclusion of more indium ions due to the structural disorder causes more scattering of light at higher doping, as inferred from XRD.

Optical absorption coefficient of the films was estimated using Lambert’s law (Equation (7))

\[
a(h\nu) \propto (h\nu - E_g)^{1/2} \tag{7}
\]

The band gap (\(E_g\)) values of the films were estimated using the Tauc plot, as shown in Figure 4(c). Figure 4(c) shows the variation of \((ah\nu)^{2}\) with \(h\nu\) for various films; moreover, the band gap values were calculated using extrapolation of straight-line portion to the x-axis of the plot (see inset of Figure 4(c)). We see that the bandgap initially increases up to 3.33 eV with increasing indium concentration till 2.5 wt\%, and then it decreases to 3.29 for 7.5 wt\% of In. The reduction in band gap at higher doping concentration indicates the disorder created in the crystalline lattice due to the higher ionic radius of In compared to Zn. The increase in band gap due to doping is expected because the charge carrier density can be increased by the increase of doping concentration, which fills the lowest states in the conduction band, causing the widening of the bonds. However, it decreases at higher doping concentration because of poor crystallinity. The band gap increase due to In doping indicates the increase of carrier concentration due to indium ions. The decrease of band gap at higher In doping concentrations is attributed to the interstitial In impurities facilitating recombination centers formed at higher doping concentrations [34].

For the increase of bandgap upto 2.5 wt\% of In concentration, the crystalline improvement and carrier concentration increase might be the reason, whereas for the decrease of band gap after 5 wt\% is due to crystalline defects produced due to interstitial In impurities at increased In concentration. The bandgap decrease due to the increase of carrier concentration may be also attributed to Burstein–Moss shift [20,35].

The impurity-dependent properties and defect states of thin films can be analyzed using photoluminescence (PL) study – a nondestructive technique. The room temperature PL spectra obtained using He–Cd laser with 325 nm excitation for different In concentrations incorporated ZnO thin films is displayed in Figure 4(d). It shows peaks at 396 nm, 415 nm, 438 nm, 476 nm, and 526 nm indicating near band edge and defect emissions. The peak at 396 nm attributes the near band edge emission (NBE). Moreover, the peaks at 415 nm and 438 nm corresponds to the Zn interstitial and vacancy-related emissions, respectively. The other peaks – 476 nm and 526 nm – caused from the defect-mediated electronic transition-based emissions. Furthermore, indium inclusion has increased the intensity of the peaks, indicating the creation of defect and trap centers. The PL study also suggests that crystalline quality decreases with increasing defects of the films for increasing In doping concentrations [23].

Raman analysis is also a useful way to examine the structural and defect variations in semiconductor materials. ZnO has a \(C_{6v}\) symmetry group due to its hexagonal wurtzite structure. The optical modes of ZnO are calculated using the following relation:

\[
\Gamma_{\text{opt}} = A_1 + 2B_2 + E_1 + 2E_2 \tag{8}
\]

where \(A_1\) and \(E_1\) denote the longitudinal optical (LO) and transversal optical (TO) modes, respectively. Moreover, \(A_1\), \(E_1\), and \(E_2\) are first-order Raman-active modes. The typical Raman spectra obtained for the different In-doped ZnO thin films coated on glass substrates are shown in Figure 5. It shows peaks at 332 cm\(^{-1}\), 384 cm\(^{-1}\), 438 cm\(^{-1}\), 582 cm\(^{-1}\), 670 cm\(^{-1}\), and 785 cm\(^{-1}\). \(E_2\) (438 cm\(^{-1}\)) is the wurtzite ZnO characteristics peak. This highly intense \(E_2\) peak of all doped and undoped films indicates the growth of quality crystalline ZnO films. Moreover, this peak intensity for 2.5% In-doped film is higher than all other films, which shows the crystallinity improvement at 2.5% indium concentration. The forbidden mode observed at 332 cm\(^{-1}\) shows the second-order \(E_2\)(high) and \(E_1\)(low) phonons. The 582 cm\(^{-1}\) peak is due to the A1 (LO) and E1(LO) vibration modes, indicating the intrinsic lattice defects produced by doping effects. The other peaks observed may be attributed to the In\(_2\)O\(_3\) defect-related modes. Moreover, the peak 438 cm\(^{-1}\) is slightly shifted to
higher angles (440 cm⁻¹) for the indium concentration of 2.5%, indicating the effect of indium doping in the phonon mode of ZnO [36,37].

### 3.4. Electrical characterization

To understand electrical properties and effect of In, the prepared films were characterized using Hall-Effect measurements. Keithley interactive digital sourcemeter (Model-2450) was used for the Hall Effect measurements under van der Pauw configuration at room temperature. The measured electrical resistivity, carrier concentration and mobility of In:ZnO films for different In concentrations are shown in Figure S3. It shows decrease of resistivity and increase of carrier concentration for the increase of In concentration indicating crystalline improvement due to incorporation of In ions into ZnO lattice as witnessed by XRD results. There is a large decrease in resistivity up to 2.5 wt% of In concentration. Mobility also decreased initial with In ions incorporation, but at higher doping concentration it is increased slightly due to structural changes as shown in XRD. When the particle size is reduced, its grain boundary scattering can cause decrease of mobility, however, depending on carrier concentration it can vary.

### 3.5. Photosensing properties

The prepared ZnO films of different indium doping concentrations were studied for their optical sensing properties. Figure 6 shows the photocurrent–voltage (I–V) plots of the undoped and various In-doped ZnO films observed under dark, and 5 mW light illuminated conditions. All the I–V plots observed from −5 V to +5 V potential range display a symmetric linear I–V variation, indicating the ohmic nature of the contacts. Moreover, all the films show a higher current under optically illuminated conditions than dark conditions, which shows the photosensing property of the fabricated devices. The ON/OFF ratios (light/dark currents) of the devices at 5 V bias were 2.8, 10.8, 3.4, and 2.4 for 0, 2.5, 5.0, and 7.5 wt% indium concentrations, respectively; however, its corresponding dark currents were increased to 0.13, 0.47, 1.0, and 0.95 µA, respectively. In-doped ZnO films show a higher current than pure ZnO, in which 2.5% of In-doped films have produced higher current than other concentrations. This higher photocurrent and ON/OFF ratio of 2.5% In-doped ZnO device implies improved film quality in terms of crystallinity and conductivity. Moreover, the increase in dark current with the increasing indium concentration indicates the decrease in resistivity shown in Hall-Effect measurements, it is due to the inclusion of In into the ZnO lattice, which liberates extra free electrons into the conduction band.

Transient response and photoswitching effect of the films prepared with various In concentrations were also studied by applying constant 5 V bias. Figure 7 displays the photocurrent variations for five consecutive ON/OFF cycles of various light intensities (1–5 mW), indicating the linear increase in current with the illuminating power. Furthermore, it shows fast recovery and quick response of the devices, showing their suitability for photosensing applications.
Moreover, as inferred from other studies, the 2.5% In-doped device displays a higher current with sharp response and recovery responses than the undoped and other higher indium-doped devices.

Figure 8(a) shows the device’s comparative recovery and responses at 3 mW intensity of light illumination. It shows a high ON current with a sharp response of the device fabricated with 2.5% indium concentration, proving the effect of 2.5% indium doping on photosensing efficiency. Such excellent response and recovery suggest its suitability for photosensing applications. The other parameters, such as photoresponsivity ($R$), external quantum efficiency ($EQE$), and detectivity ($D^*$) of the photosensor
devices for different indium doping concentrations, were calculated using Equations (8), (9), and (10). The values of the different parameters are shown in Figure 8(b) [38].

\[ R = \frac{I_p}{P_m \times A} \]  
\[ EQE = \frac{hc}{e\lambda} \]  
\[ D' = R \sqrt{\frac{A}{2el_{dark}}} \]

where \( A \) denotes an active area, \( P_m \) represents incident light intensity, and \( I_p \) denotes photocurrent; moreover, \( l_{(ph-dark)} \) and constants \( e, c, h, \) and \( \lambda \) have their usual meanings. Figure 8b shows that the 2.5% indium-doped device shows excellent performance regarding all the parameters, indicating its usefulness.

A heterostructure photodiode was constructed by coating ZnO film with 2.5% indium concentration onto p-type silicon using Ag metal contacts, as shown in the inset of Figure 9(a). The \( I-V \) response of the In:ZnO/p-Si heterojunction device measured at different illuminated conditions is shown in Figure 9(a). As shown in Figure 9(a), the fabricated In:ZnO/p-Si devices showed higher photoresponse for UV light (350 nm) compared to other wavelengths indicating ZnO bandgap dependent response. This increase of current under illumination indicates photoinduced generation of carriers demonstrating the photosensing effect of fabricated heterostructure device. Responsivity and detectivity of the heterostructure calculated using UV light intensity is shown in Table 2 with comparison of literature values.

Furthermore, the asymmetric non-linear \( I-V \) nature suggests the formation of the p–n junction between In: ZnO and p-Si layers. All the \( I-V \) plots under both dark and various light intensities show a higher reverse current than forward bias, revealing the photovoltaic nature of the fabricated heterojunction In:ZnO/p-Si device. This phenomenon is further justified by the shift of minimum current position toward the positive potential, as shown in the inset of Figure 9(b) (left). The ideality factor was determined using the following relations to further examine the electrical properties of the junction (Equations (12) and (13)).

The current of the heterojunction device can be expressed as,

\[ I = I_0 \left[ \exp \left( \frac{qV}{\eta k_B T} \right) - 1 \right] \]  
\[ \eta = \frac{q}{k_B T} \left( \frac{d(V)}{d(ln(I))} \right) \]
Table 2. Comparison of obtained photoresponse values with literature.

| Materials/Structure | Responsivity (AW⁻¹) | Detectivity (Jones) | Reference |
|---------------------|----------------------|---------------------|-----------|
| In-doped ZnO        | 0.074                | –                   | [40]      |
| Nanostructure       |                      |                     |           |
| Sb-doped ZnO films  | 1000 × 10⁻³          | –                   | [41]      |
| Mn-doped ZnO NRs    | 65 × 10⁻⁵            | –                   | [42]      |
| Ga-doped ZnO        | 0.0723               | –                   | [43]      |
| ZnO/Si structure    | 0.12                 | –                   | [44]      |
| ZnO/micro-Si        | 0.14                 | 10¹⁰               | [45]      |
| n-AgNWs/ZnO:Ga      | 5.52                 | 2.34 × 10¹²         | [46]      |
| MW/p-Si             |                      |                     |           |
| ZnO                 | 121                  | –                   | [47]      |
| In-doped ZnO/Si     | 1.67                 | –                   | [39]      |
| Ga-doped ZnO/PEN    | 0.046                | 3.92 × 10¹²         | [48]      |
| ZnO@CNT             | 0.04                 | 7.1 × 10¹²          | [49]      |
| In-doped ZnO        | 0.95                 | 7.7 × 10⁷           | work      |
| In-doped ZnO/Si     | 1.07                 | 8.4 × 10⁷           | work      |

The ideality factor (η) of the ZnO thin film coated with 2.5% indium concentration was calculated by fitting a straight line to the In(J) versus V plot for the applied voltage of 0.5 V, as shown in the right inset of Figure 9 (b). We found an ideality factor of 3.76, which is higher than the standard homojunction values between 1 and 2, indicating the non-ideal diode behavior with more defect and interface states causing electron-hole recombination [39]. However, the response of this heterojunction can be improved. The rectification ratio I⁺/I⁻ of the device calculated is about 1.2 (Fig. S4), which is very low as stated for ideality factor as non-ideal diode.

4. Conclusion

Indium-doped and undoped ZnO thin films with different doping concentrations were successfully prepared on glass and p-silicon substrates using the SILAR technique. The morphological, structural, and optical properties of the grown films show the growth of well-formed indium included ZnO. Indium concentration of 2.5% has yielded enhanced structural and optical properties. Moreover, the fabricated photosensor devices exhibit all properties depending on indium-doping concentration showing excellent photosensign efficiency at 2.5% indium concentration. The photodiodes prepared using 2.5% In-doped In:ZnO/p-Si device show good response with photovoltaic nature. Both the fabricated photosensor devices exhibit improved responses for the UV region of the optical band. These results suggest that In:ZnO can be potentially be used in optoelectronic applications by properly fabricating layers and contact materials.

Article highlights

- Indium-doped ZnO thin films were prepared using SILAR method.
- Indium concentration 2.5% showed excellent structural, optical, and photosensing properties.

- In:ZnO and its heterojunction with p-Si were studied for photosensing properties.
- In:ZnO thin film coated with 2.5% of indium showed fast response and recovery times.
- Fabricated In:ZnO/p-Si heterojunction showed ideality factor of 3.76.

Disclosure statement

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References

[1] Benzitouni S, Zaabat M, Mahdjoub A, et al. High transparency and conductivity of heavily In-doped ZnO thin films deposited by dip-coating method. Mater Sci-Poland. 2018;36(3):427–434.
[2] Edinger S, Bansal N, Bauch M, et al. Highly transparent and conductive indium-doped zinc oxide films deposited at low substrate temperature by spray pyrolysis from water-based solutions. J Mater Sci. 2017;52 (14):8591–8602.
[3] Golshan Bafghi Z, Manavizadeh N. Low power ZnO nanorod-based ultraviolet photodetector: effect of alcoholic growth precursor. Opt Laser Technol. 2020 Sep;129:106310.
[4] Kathalingam A, Rhee JK. Fabrication and characterization of solution processed n-ZnO nanowire/p-Si heterojunction device. J Nanosci Nanotechnol. 2012 Sep;12(9):6948–6954.
[5] Singh G, Shrivastava S, Jain D, et al. Effect of indium doping on zinc oxide films prepared by chemical spray pyrolysis technique. Bull Mater Sci. 2010;33 (3):581–587.
[6] Gu P, Zhu X, Yang D. Structural, optical and photoelectric properties of Mn-doped ZnO films used for ultraviolet detectors. RSC Adv. 2019;9(14):8039–8047.
[7] Alsultany FH, Hassan Z, Ahmed NM, et al. Effects of ZnO seed layer thickness on catalyst-free growth of ZnO nanostructures for enhanced UV photoresponse. Opt Laser Technol. 2018 Jan;108:344–353.
[8] Salah M, Azizi S, Boukhachem A, et al. editors. Doped zinc oxide thin films for photosensors devices. 2016 7th International Conference on Sciences of Electronics, Technologies of Information and Telecommunications (SETIT): 2016, Hammamet, Tunisia: IEEE. https://ieeexplore.ieee.org/abstract/document/7939901
[9] Hannas M, Manut A, Herman S, et al. editors. Effect of indium concentration on optical and electrical properties of in doped ZnO thin films for gas sensing application. 2014 IEEE International Conference on Semiconductor Electronics (ICSEE2014); 2014, Kuala Lumpur, Malaysia: IEEE. https://ieeexplore.ieee.org/document/6920893

[10] Che louche A, Touam T, Necib K, et al. Investigation of the effects of drying process on microstructural and luminescence properties of Al-doped ZnO thin films. J Lumin. 2020 Mar 1;219:116891.

[11] I BOZ, Göktay A, Aslan F, et al. Physical properties of solution processable n-type Fe and Al co-doped ZnO nanostructured thin films: role of Al doping levels and annealing. Mat Sci Semiconductor Process. 2018;75:221-233 doi:10.1016/j.mssp.2017.11.033

[12] Mikalzade F, Türkän H, Önal F, et al. Structural and magnetic properties of polycrystalline Zn1−xMnxO films synthesized on glass and p-type Si substrates using Sol–Gel technique. Appl Phys A. 2021 May 12;127(6):408.

[13] Kim MS, Yim KG, Kim S, et al. Growth and characterization of indium-doped zinc oxide thin films prepared by sol-gel method. Acta Physica Polonica-Series A General Phys. 2012;121(1):217.

[14] Jellal I, Nouneh K, Taura H, et al. Enhanced photocatalytic activity of supported Cu-doped ZnO nanostructures prepared by SILAR method. Opt Mater. 2021 Jan 1;111:110669.

[15] Anbuselvan D, Nilavazhagan S, Santhanam A, et al. The effect of iron doping on the structural, optical, surface morphological, and temperature-dependent magnetic properties of ZnO nanoparticles. J Phys. 2020;33(9):094001.

[16] Anand V, Sakhthivelu A, Kumar KDA, et al. Novel rare earth Gd and Al co-doped ZnO thin films prepared by nebulizer spray method for optoelectronic applications. Superlattices Microstruct. 2018;123:311-322.

[17] Arshad M, Meenaz Ansari M, Ahmed A5, et al. Band gap engineering and enhanced photoluminescence of Mg doped ZnO nanoparticles synthesized by wet chemical route. J Lumin. 2015 May 1;161:275-280.

[18] Gherab K, Al-Douri Y, Hashim U, et al. Fabrication and characterizations of Al nanoparticles doped ZnO nanostructures-based integrated electrochemical biosensor. J Mater Res Technol. 2020 Jan 1;9(1):857–867.

[19] Alsaad A, Ahmad A, Qattan I, et al. Structural, optoelectrical, linear, and nonlinear optical characterizations of dip-synthesized undoped ZnO and group III elements (B, Al, Ga, and In)-doped ZnO thin films. Crystals. 2020;10(4):252.

[20] Goktas A, Tumbul A, Aba Z, et al. Mg doping levels and annealing temperature induced structural, optical and electrical properties of highly c-axis oriented ZnO: Mg thin films and Al/ZnO: Mg/p-Si/Al heterojunction diode. Thin Solid Films. 2019;680:20–30.

[21] Bergum K, Fjellvåg H, Nilsen O. Thickness dependent structural, optical and electrical properties of Ti-doped ZnO films prepared by atomic layer deposition. Appl Surf Sci. 2015;332:494–499.

[22] Tonny KN, Rafique R, Sharmin A, et al. Electrical, optical and structural properties of transparent conducting Al doped ZnO (AZO) deposited by sol-gel spin coating. AIP Adv. 2018;8(6):065307.

[23] Pati S, Banerji P, Majumder S, et al. Properties of indium doped nanocrystalline ZnO thin films and their enhanced gas sensing performance. RSC Adv. 2015;5(75):61230–61238.

[24] Hafdallah A, Yanieb F, Aida M, et al. In doped ZnO thin films. J Alloys Compd. 2011;509(26):7267–7270.

[25] Saltabaye V, Yildirim MA, Ates A, et al. The effect of indium doping concentration on structural, morphological and gas sensing properties of IZO thin films deposited SILAR method. Mater Sci Semiconductor Process. 2019 Oct 1;101:28–36.

[26] Musavi E, Khanlary M, Khakpour Z. Red-Orange photoluminescence emission of sol-gel dip-coated prepared ZnO and ZnO:Al nano-crystalline films. J Lumin. 2019 Dec 1;216:116696.

[27] Li C, Yu L, Yuan X, et al. Ag nanorods assembled with ZnO nanowalls for near-linear high-response UV photodetectors. J Alloys Compd. 2020;830:154652.

[28] Kumar KDA, Valanarasu S, Ganesh V, et al. Effect of precursors on key opto-electrical properties of successive ion layer adsorption and reaction-prepared Al: zno thin films. J Electron Mater. 2018;47(2):1335–1343.

[29] Raïdou A, Lharch M, Nouneh K, et al., editors. Effect of substrate on ZnO thin films grown by SILAR method. 2014 International Renewable and Sustainable Energy Conference (IRSEC); 2014. Ouarzazate, Morocco: IEEE. https://ieeexplore.ieee.org/abstract/document/7059829

[30] Zhou B, Chen L, Li C, et al. Significant enhancement in the thermoelectric performance of aluminum-doped ZnO tuned by pore structure. ACS Appl Mater Interfaces. 2020;12(46):51669–51678.

[31] Biswal R, Maldonado A, Vega-Pérez J, et al. Indium doped zinc oxide thin films deposited by ultrasonic chemical spray technique, starting from zinc acetylacetone and indium chloride. Materials. 2014;7(7):5038–5046.

[32] Chen K, Hung F-Y, Chang S-J, et al. Microstructures, optical and electrical properties of In-doped ZnO thin films prepared by sol–gel method. Appl Surf Sci. 2009;255(12):6308–6312.

[33] Mohammadiharebbagh R, Pat S, Özmen S, et al. Investigation of the optical properties of the indium-doped ZnO thin films deposited by a thermionic vacuum arc. Optik. 2018;157:667–674.

[34] Shaheera M, Girija K, Kaur M, et al. Characterization and device application of indium doped ZnO homo-junction prepared by RF magnetron sputtering. Opt Mater. 2020;101:109723.

[35] Sahoo B, Behera D, Pradhan SK, et al. Analysis of structural, optical and electrical properties of nano-particle indium doped zinc oxide thin films. Mater Res Express. 2019 Oct 18;6(11):1150a6.

[36] Ngo-Duc T, Singh K, Meyyappan M, et al. Vertical ZnO nanowire growth on metal substrates. Nanotechnology. 2012;23(19):194015.

[37] Cerqueira M, Viseu T, Ayres de Campos J, et al. Raman study of insulating and conductive ZnO(AI, Mn) thin films. Phy Stat Solidi (A). 2015;212(10):2345–2354.

[38] Kathalingam A, Valanarasu S, Ahamad T, et al. Spray pressure variation effect on the properties of CdS thin films for photodetector applications. Ceram Int. 2021;47(6):7608–7616.
The improvement photoresponsivity of ZnO based photodiode with indium doping. Süleyman Demirel Üniversitesi Fen Bilimleri Enstitüsü Dergisi. 2020;24(1):178–187.

Young S-J, Liu Y-H. Ultraviolet photodetectors with 2-D indium-doped ZnO nanostructures. IEEE Trans Electron Devices. 2016;63(8):3160–3164.

Mohite S, Rajpure K. Synthesis and characterization of Sb doped ZnO thin films for photodetector application. Opt Mater. 2014;36(4):833–838.

Chey CO, Liu X, Alnoor H, et al. Fast piezoresistive sensor and UV photodetector based on Mn-doped ZnO nanorods. Physica Status Solidi (RRL)–Rapid Research Letters. 2015;9(1):87–91.

Young S-J, Liu Y-H. Ultraviolet photodetectors with Ga-doped ZnO nanosheets structure. Microelectron Eng. 2015;148:14–16.

Periasamy C, Chakrabarti P. Large-area and nanoscale n-ZnO/p-Si heterojunction photodetectors. J Vacuum Sci Technol B Nanotechnol Microelectron. 2011;29(5):051206.

Chatzigiannakis G, Jaros A, Leturcq R, et al. Laser-microstructured ZnO/p-Si photodetector with enhanced and broadband responsivity across the ultraviolet–visible–near-infrared range. ACS Appl Electron Mater. 2020;2(9):2819–2828.

Liu Y, Dai R, Jiang M, et al. Enhanced luminescence/photodetecting bifunctional devices based on ZnO: Ga microwire/p-Si heterojunction by incorporating Ag nanowires. Nanoscale Adv. 2021;3(19):5605–5617.

Elkamel IB, Hamdaoui N, Mezni A, et al. High responsivity and 1/f noise of an ultraviolet photodetector based on Ni doped ZnO nanoparticles. RSC Adv. 2018;8(56):32333–32343.

Young S-J, Liu Y-H, Shiblee MNI, et al. Flexible ultraviolet photodetectors based on one-dimensional gallium-doped zinc oxide nanostructures. ACS Appl Electron Mater. 2020;2(11):3522–3529.

Choi M-S, Park T, Kim W-J, et al. High-performance ultraviolet photodetector based on a zinc oxide nanoparticle@ single-walled carbon nanotube heterojunction hybrid film. Nanomaterials. 2020;10(2):395.