Nickel Doped Zinc Oxide Thin Films for Visible Blind Ultraviolet Photodetection Applications

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The current research aims to investigate the effect of nickel doping on the structural and opto-electrical characteristics of zinc oxide thin films. Sol-gel spin coating technique has been utilized to deposit Zn0-xNixO (x = 0, 0.005, 0.010, and 0.015) films on glass substrates. X-ray diffraction (XRD) analysis confirms the formation of crystalline zinc oxide thin films with hexagonal wurtzite structure. Williamson-Hall analysis has been performed to study the individual contribution of lattice strain and crystallite size to the peak broadening in the XRD pattern. Scanning electron microscopy (SEM), Photoluminescence spectroscopy, and UV–visible spectroscopic techniques have been used to examine the surface morphology and optical properties of the deposited films. Transient photocurrent measurements have been performed on all the films under the exposure of ultraviolet (UV) light of wavelengths 365 and 254 nm with on/off cycle of 100 s, and various device key parameters such as sensitivity, responsivity, and quantum efficiency, etc have been determined. Sensitivities of the fabricated photodetectors (PDs) are found to be 5463%, 3809%, 3100%, and 831% for pristine ZnO, Zn0.995Ni0.005O, Zn0.99Ni0.01O, and Zn0.985Ni0.015O, respectively. The UV photodetection mechanism, which is based on the interaction between chemisorbed oxygen on the surface of ZnO and photo-generated holes, has been thoroughly discussed.

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Experimental Details

During the past few decades, plethora of global energy consumption has accelerated the research towards the development of sustainable and energy-efficient photodetectors. Recently, considerable attention has been paid to ultraviolet (UV) photodetectors (PDs) owing to their widespread implementation in the scientific, military, and medical sectors.1–4 UV photodetectors are widely employed for human body protection.5,6 Such detectors are necessary to reduce UV radiation exposure, which may harm the human beings and cause skin cancer, impair the immune system, and hasten the aging process. Although, a wide range of silicon-based UV photodetectors with high sensitivity, high signal-to-noise ratio, and fast response are available, but these detectors have some limitations, which include the need of visible and infrared light filters for spectral selectivity, a high degradation rate, and low efficiency,7 etc. Implementation of wide bandgap semiconducting materials and the devices based on such materials have revolutionized various sectors of society, and the researchers, all over the world, are still working on these materials to enhance the performances of related devices. Because of their combined opto-electrical capabilities, semiconducting metal oxides are the potential materials for emerging optical and electrical applications.8–10 Among them, zinc oxide (ZnO) is a well-known metal oxide with excellent multifaceted properties like wide direct bandgap energy of 3.37 eV, existence in n-type semiconductor behavior, and exciton binding energy of 60 meV at room temperature. It is a useful material for UV photodetection applications because of its high radiation endurance, low toxicology, high transparency with electron mobility, low cost, and flexibility of fabrication via a number of preparation techniques.10–12 Furthermore, pristine and doped ZnO thin films have a wide range of technological applications in light emitting diodes (LEDs), gas sensors, photocatalysts, solar cells, and other photonic devices.13–17 Sol–gel18,19 technique, chemical vapor deposition (CVD),20 electron beam evaporation,21 sputtering,22 pulsed laser deposition (PLD),23 and chemical bath methods (CBD)24 are among the most common deposition processes used to fabricate the ZnO thin films. In fact, the photovoltaic properties are greatly dependent on the fabrication process. It should also be noted that the key requirements for the fabrication of photodetectors is repeatability, adaptability, and low-cost production of materials. The electrical functionality of ZnO does not lose even in the solution state, which opens avenues to fabricate the films by simple and cost-effective chemical routes, viz., chemical bath deposition, sol-gel spin coating, etc. All these processes are low-temperature and thin film can be deposited on a large scale on various substrates. We have employed a low-cost sol-gel spin coating approach to deposit the ZnO and Ni-doped ZnO thin films. Sol-gel spin coating is a unique and straightforward method of generating many types of nanostructures with control over deposition rate, temperature, growth level, and thickness, along with various other parameters. We have investigated the effect of various Ni doping concentrations (0, 0.5, 1, 1.5%) on the morphological, structural, optical, and photoelectric/or photodetection properties of nanostructured ZnO thin films.

Zinc acetate di-hydrate (Hi-media) and Diethanolamine (Hi-media) were used as precursors and sol stabilizer, respectively. Nickel acetate (Sigma Aldrich) was used as the source of nickel atoms. All the chemicals used were of analytical grade and were utilized without any additional purification. Equimolar solutions (0.4 M) of zinc acetate and Diethanolamine (DEA) were prepared by dispersing a suitable quantity of Zn(CH3COO)2·2H2O and DEA in 30 ml 2-propanol. The whole process of thin film deposition and device fabrication is shown in schematic Fig. 1.

The solution was stirred on a magnetic stirrer for 1 h before being left to age for 24 h. Similarly, three more solutions were prepared using 0.5, 1, and 1.5 molar percentage of nickel acetate. Glass substrates were degreased by ultra-sonication in detergent, hydrochloric acid, and acetone, alternatively. Finally, the glass substrates were washed with de-ionized water and dried in a hot air oven. Aged sol was spin-coated over a glass substrate at the rotation speed of 1500 rpm, and after each coating film was dried at 120 °C. Five coats of each sol were deposited on different glass substrates. All the deposited films were annealed at 550 °C in a tubular furnace in the ambient environment. For photocurrent measurement, devices were fabricated by depositing two parallel aluminum electrodes by the thermal evaporation technique. The chamber was kept at a vacuum of 10−5 torr during the deposition.

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The phase composition and structure of annealed films were investigated using an X-ray diffraction pattern recorded on a Rigaku MiniFlex–600 diffractometer equipped with monochromatic Cu-Kα radiation (\(\lambda = 1.54056 \text{ Å} \)) at a scan rate of 1° min\(^{-1}\) and a step size of 0.02°. The morphology of the deposited films was studied using a high-resolution scanning electron microscope (ZEISS model Evo 18) at a magnification of 50kX and accelerating potential of 20 kV. The elemental compositions were quantified using an energy dispersive X-ray spectroscopy (EDAX make Oxford instruments equipped with X-act-10mm\(^2\) SDD Detector) fitted with the afore mentioned SEM setup. The optical properties of the deposited films have been recorded over Horiba instruments made sophisticated fluorescence spectrometer (FL3C-21). All electrical measurements were done in MSM (metal-semiconductor-metal) geometry. Ultraviolet (UV) photodetection measurements were accomplished on Keithley’s 617 electrometer interfaced with the Lab-View program through GPIB cable. Monochromatic UV sources of wavelengths 365 nm and 254 nm were used to illuminate the devices during these measurements.

**Results and Discussion**

Figure 2 depicts the X-ray diffraction patterns of pristine and nickel-doped zinc oxide thin films. The formation of a hexagonal wurtzite-structured ZnO thin film is confirmed by the perfect similarity of the XRD spectra with JCPDS card # 80–0075\(^{26–28}\). All of the observable peaks can be correlated to the wurtzite hexagonal structure shown in Fig. 2. The absence of any extra peak in the XRD pattern of doped ZnO film confirms the incorporation of nickel atoms in the ZnO crystal lattice. It is obvious that the intensity of the peaks in the Ni-doped thin films is lower than that of the undoped (pure) ZnO film. This drop in the intensity of the diffraction peaks of the Ni-doped thin film shows that Ni doping has severely reduced the crystalline character of the ZnO thin films. The observed shift in XRD peaks can be explained in terms of small ionic radius of Ni\(^{2+}\) as compared to Zn\(^{2+}\).

The following equations have been used to determine unit-cell parameters \(a, c\) and volume in accordance with the wurtzite hexagonal structure:\(^{29}\)

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

\[
V = \frac{\sqrt{3}}{2} a^2 c \tag{2}
\]

Where \(d_{hkl}\) is inter-planer spacing for respective miller indices, \(a\) and \(c\) are lattice parameters of the hexagonal crystal lattice. All the calculated parameters are approximately equal to as given in JCPDS card # 80–0075. The ionic radius of Ni\(^{2+}\) is 69 pm, while that of Zn\(^{2+}\) is 74 pm. Table I clearly shows that the value of lattice parameters continues to decrease due to the small ionic radius of Ni\(^{2+}\) ions.

**Williamson-Hall size-strain analysis.** — The Williamson-Hall (W–H) technique may be used to analyze an XRD pattern to calculate the crystallite size and lattice strain. However, crystallite size can also be calculated by Scherrer’s method but it is less
accurate as compared to the W–H method because it does not eliminate the effect of peak widening caused by lattice strain. The W–H approach individually addresses peak broadening caused by crystallite size (β), and lattice strain (ε), providing a value for both that is substantially more accurate. 

\[
\beta_{bl} = \beta_\varepsilon + \beta_d
\]  

\[
\beta_{bl} = \left( \frac{k\lambda}{D \cos \theta} \right) + (4e \tan \theta)
\]

Here, \(\beta_{bl}\) is the full-width at half maximum (FWHM), k is constant having a value of 0.94, \(\lambda\) is the wavelength of X-ray, which is 1.54056 Å for Cu-Kα, \(\varepsilon\) is lattice strain and \(D\) is crystallite size. 

Now, straight line fitting of 4sin\(\theta\) vs \(\beta_{cos\theta}\) curve, may be used to directly determine crystallite size (D) and lattice strain (ε) as shown in Fig. 3.

W–H plot has been plotted for pristine ZnO thin film using five prominent peaks from the XRD pattern. Crystallite sizes calculated by linear fitting of W–H plots for \(x = 0, 0.005, 0.01, \text{and } 0.015\) are found to be 14.83, 17.23, 19.3, and 25.63 nm, respectively, and lattice strains are 8.98, 14.83, 17.23, 19.3, and 25.63 nm, respectively, and by linear fitting of W–H method because it does not eliminate the effect of peak widening caused by lattice strain. The W–H approach individually addresses peak broadening caused by crystallite size (β), and lattice strain (ε), providing a value for both that is substantially more accurate. 

### Table I. Lattice parameters (a and c) and unit cell volume of the pristine and doped ZnO thin films.

| Sample                  | ZnO        | Zn_{0.99}Ni_{0.005}O | Zn_{0.99}Ni_{0.01}O | Zn_{0.99}Ni_{0.015}O |
|------------------------|------------|-----------------------|---------------------|-----------------------|
| Lattice parameter “a” (Å) | 3.24       | 3.21                   | 3.19                | 3.19                  |
| Lattice parameter “c” (Å) | 5.19       | 5.16                   | 5.15                | 5.15                  |
| Unit cell volume “V” (Å³) | 47.18      | 46.04                  | 45.38               | 45.37                 |

### Optical properties

The optical characteristics of pristine and Ni-doped ZnO thin films become increasingly prominent when particle size is pushed to the nanoscale. UV–visible spectroscopy has been used to comprehensively evaluate the optical properties of pure and Ni-doped ZnO thin films. Since different dopants can produce different crystal defects in the ZnO crystal structure, the band gap of these compound semiconductor nanoparticles varies accordingly. Figure 5 depicts the UV–Visible transmission spectra of the pure and Ni-doped ZnO thin films deposited over the glass substrates. The transmission spectra of the deposited films have been recorded over the wavelength range from 300 to 800 nm. The deposited films are found to be almost transparent to the radiations in the 400 to 800 nm wavelength range with a transmittance greater than 96%. When compared to pristine ZnO, the absorption edge of Ni-doped ZnO thin films exhibits substantial blue shift. Because of the inclusion of Ni ions, the observed blue shift suggests a change in the band structure in Ni-doped ZnO films. Bandgap value for the films having Ni content 0, 0.5, 1, and 1.5% is found to be 3.41, 3.45, 3.46 and 3.48 eV, respectively. The observed trend in bandgaps with an increase in Ni content is in good agreement with many published reports. Band gaps are observed to increase with an increase in the nickel concentration as shown in the insets of Fig. 5. The size effect is unlikely to be responsible for the observed blue shift because the diameters of the produced nanostructures are higher than the excitonic Bohr radius in ZnO. The band structure modification might be caused by the sp-d exchange interaction between ZnO band electrons and localized d-electrons associated with doped Ni^{2+} cations. The widening of the optical energy band gap and the blueshift of the absorption edge can also be attributed to an increase in carrier concentration and are explained in theory by the Moss-Burstein band filling phenomena, which is commonly observed in n-type semiconductors.

The optical properties of the deposited films have been further investigated by Photoluminescence spectra in the wavelength range 400–550 nm, as shown in Fig. 6. Each PL spectrum of the pristine as well as the Ni-doped ZnO films consist of two sharp peaks around 413 and 437 nm and a broad peak around 464 nm. Strong UV peak around 413 nm apparently originates from recombination of free excitons. The main feature is an evident decrease of the UV peak intensity with Nickel doping, which indicates a decrease in the recombination rate of the photogenerated carriers, and this may result from the doped Ni^{2+} ions that act as traps to capture the photogenerated electrons or holes. Most likely, the low intensity visible emissions are linked with the vacancies in the singly ionised oxygen compounds that emerge from photogenerated recombination. It appears that additional defects in the nanoparticles sample may be generated as a result of the inclusion of dopants into the ZnO lattice. Hence, the doping of Ni into the ZnO lattice significantly weakens the band edge emission and increases the visible emission. Holes are recombined with electrons from oxygen vacancies.

### Photodetection performance

Photodetection measurements have been performed on the fabricated devices by exposing them to UV light of wavelengths 365 and 254 nm at a fixed applied bias of 5 V. Transient photoresponse of the devices have been recorded over on/off cycles of 100 s each. All the cycles have been recorded over the fixed intensity of 0.979 mW cm\(^{-2}\) of UV light and the effective areas of the devices have been kept 0.215 cm\(^2\).
To check the repeatability of fabricated devices five cycles of transient photoresponse have been recorded and it has been found that all the devices have a regenerative response, which is the main requirement for a photodetector. The charge carriers transit in zinc oxide are controlled by oxygen molecules adsorbed on the film surface, which withdraw electrons from the metal oxide semiconductor’s conduction band to generate oxygen ions. This causes a drop in charge carrier concentration and is responsible for poor conductivity in metal oxides. The surface-adsorbed oxygen molecules at the grain boundaries produce a depletion zone that is susceptible to upward band bending or the creation of a potential barrier. The extent of band bending depends upon the width of depletion layer at the grain boundaries.

When exposed to UV light, the photogenerated electron-hole pairs are either adsorbed by the oxygen molecules or gathered at the electrodes. While electrons are responsible for increased photocurrent through a reduction in potential barrier height and the size of the space-charge region at the grains and grain boundaries, photogenerated holes interact with oxygen ions on the film surface. Thus, the degree of band bending or change in potential barrier height in UV light controls the photo-response in the metal oxide semiconductor films.40–43

Parameters of Photodetector’s Performance.—There are some parameters which are commonly used to assess a photodetector’s performance. Here, we have calculated and discussed some of them. Photoreponse factor (S) or sensitivity of a photodetector is the percentage change in current on UV exposure relative to dark current.

**Figure 4.** SEM microgram of (a) pristine ZnO, (b) Zn_{0.995}Ni_{0.005}O, (c) Zn_{0.99}Ni_{0.01}O, and (d) Zn_{0.98}Ni_{0.015}O at the magnification of ×500000.

**Figure 5.** UV–Visible transmission spectra of Zn_{1−x}Ni_{x}O (x = 0, 0.005, 0.010, and 0.015).

**Figure 6.** Photoluminescence spectra of the deposited films.
Sensitivity II = \frac{(I_p - I_d)}{I_d} \times 100 \quad [5]

Transient photoresponse of the deposited films have also been recorded under the exposure of UV light of wavelength 254 nm (Figs. 7a–7d). The sensitivity values of the deposited films are found to be 2422, 1831, 1358 and 618% for pristine ZnO, Zn0.995Ni0.005O, Zn0.99Ni0.01O, and Zn0.985Ni0.015O, respectively, when exposed to 254 nm UV radiations.

Responsivity is another parameter used to measure the device’s sensitivity toward the intensity of incident light. It is the ratio of obtained output current to the incident power density. Mathematically, it can be calculated by the following relation:

\text{Responsivity} = \frac{(\Delta I)}{P_d} \times A \quad [6]

Where, \(P_d\) is the intensity of incident light, and \(A\) is the effective area or area between the parallel electrodes. Under the exposure of UV light (365 nm) of intensity 0.979 mW cm\(^{-2}\), responsivity values of ZnO, Zn0.995Ni0.005O, Zn0.99Ni0.01O and Zn0.985Ni0.015O thin films are found to be 7.031 \times 10^{-5}, 4.89 \times 10^{-5}, 3.94 \times 10^{-5} and 1.04 \times 10^{-5} A W^{-1}, respectively. Responsivity also shows the same trend as that of sensitivity. However, it is much greater than as reported by Elkamel et al.\textsuperscript{50} for Ni-doped ZnO nanoparticles.

External quantum efficiency (EQE) is another measure used to determine the photodetector’s response to incident light. It is commonly termed as photon to electron conversion efficiency. It is the number of charge carriers created by a single incident photon. It can be estimated as follows:

\text{EQE} = \frac{R_{\lambda} h c}{e \lambda} \quad [7]

Where, \(R_{\lambda}\) is responsivity, \(h\) is Planck’s constant (\(=6.62 \times 10^{-34}\) J.s), \(c\) is the velocity of light (\(=3 \times 10^8\) m s\(^{-1}\)), \(e\) is the electronic charge (\(=1.6 \times 10^{-19}\) C), and \(\lambda\) is the wavelength of the incident UV light (\(= 365\) nm or 254 nm).
The observed values of EQE in the present study are $2.39 \times 10^{-4}$, $1.66 \times 10^{-4}$, $1.34 \times 10^{-4}$, and $3.55 \times 10^{-5}$ for pristine ZnO, Zn$_{0.995}$Ni$_{0.005}$O, Zn$_{0.99}$Ni$_{0.01}$O, and Zn$_{0.985}$Ni$_{0.015}$O thin films, respectively under exposure of UV wavelength of wavelength 365 nm.

As soon as the device is exposed to UV light, it takes a while to attain its maximum photocurrent value; similar behavior is observed on switching off the light. The transient photocurrent of a photodetector can be expressed by the following equation

$$I_t = I_e + A e^{-t/t_o}$$

Here, $t_o$ is the time constant and gives us an idea about the temporal response of the device. Transient photoresponse of the fabricated devices was also recorded under the illumination of UV light of wavelength 254 nm and shown in Fig. 8.

Single cycle of photocurrent under the exposure of UV light (365 nm) of intensity 0.979 mW cm$^{-2}$ was fitted exponentially (Fig. 9) using Eq. 8. Obtained values of rise and decay time are given in Table III. It is found that the prepared photodetectors have a comparatively long decay time when compared to their rising time. The large decay time may be due to the time taken by surface valances to re-adsorb the oxygen molecule.

### Conclusions

In summary, the sol-gel spin coating process has been used to deposit pristine ZnO and Ni (0.5, 1, and 1.5 wt%) doped ZnO thin films on glass substrates. Crystalline forms with hexagonal wurtzite phase of the deposited films have been confirmed using XRD analysis. Crystallite sizes have been calculated using Williamson-Hall approach, which are found to be 14.83,
17.23, 19.30, and 25.63 nm, respectively. Moreover, the lattice strains for $x = 0.005, 0.010$ and $0.015$ films are determined as $8.98 \times 10^{-5}$, $-2.42 \times 10^{-5}$, $-3.44 \times 10^{-5}$, and $-7.51 \times 10^{-5}$ respectively. Sensitivities of the fabricated PDs are found to be $5463\%$, $3809\%$, $3100\%$, and $831\%$ for pristine ZnO, $\text{Zn}_0.995\text{Ni}_{0.005}\text{O}$, $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$, and $\text{Zn}_{0.985}\text{Ni}_{0.015}\text{O}$ respectively, under 365 nm UV radiations. Responsivities of the fabricated PDs at the fixed intensity of $\sim 0.979 \text{ mW cm}^{-2}$ for UV light of wavelength 365 nm, are $7.031 \times 10^{-5}$, $4.89 \times 10^{-5}$, $3.94 \times 10^{-5}$ and $1.04 \times 10^{-5}$ $\text{A W}^{-1}$ for ZnO, $\text{Zn}_0.995\text{Ni}_{0.005}\text{O}$, $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$, and $\text{Zn}_{0.985}\text{Ni}_{0.015}\text{O}$ thin films, respectively. EQE of PDs under discussion are observed as $2.39 \times 10^{-4}$, $1.66 \times 10^{-4}$, $1.34 \times 10^{-4}$, and $3.55 \times 10^{-4}$ for pristine ZnO, $\text{Zn}_0.995\text{Ni}_{0.005}\text{O}$, $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$, and $\text{Zn}_{0.985}\text{Ni}_{0.015}\text{O}$ thin films, respectively.

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