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RESEARCH ARTICLE

THE INFLUENCE OF NI DOPING ON THE STRUCTURAL, OPTICAL AND MORPHOLOGICAL PROPERTIES OF ZNO THIN FILMS GROWN BY SILAR METHOD

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ABSTRACT

The influence of Ni doping on the structural, optical and morphological properties of ZnO thin films grown by SILAR method are discussed in detail. The diffraction XRD patterns reveal good crystalline quality without any appreciable changes from pure ZnO films and are genuinely polycrystalline with a hexagonal wurtzite structure. The observed 'd' spacing values are in good agreement with the standard values of ZnO. X-ray diffraction results provide the evidence that Ni is incorporated into the ZnO lattice at Zn site. Also ZnO films with (*002*) texturing is a promising candidate for solar cells, photo detectors, light-emitting devices, thin film transistors and surface acoustic wave guide applications. The optical properties revealed a decrease of band gap with Ni doping. The morphological changes evinced are also reported. The studies reveal that microstructure and optical properties may be tailored with a limited extent of Ni doping by SILAR mthod.

INTRODUCTION

ZnO is of immense interest because of its low-voltage and short wavelength electro-optical devices including light emitting diodes and laser devices due to its wide band-gap (3.37 eV at room temperature) and large exciton binding energy (60 meV). An array of hierarchical assembly of nanoscale building blocks such as nanocantilever, nanocombs (NCs), is a crucial step toward realization of functional nanosystems and represents a significant challenge in the field of nanoscale science [1]. In this regard, many papers have recently reported fabrication of ZnO nanocantilever and NCs [2]. For example, Yang's research group [2] has reported ZnO of room-temperature ultraviolet nanowire nanolasers and dendritic nanowire ultraviolet laser array. Wang and co-workers [3] have synthesized ZnO nanocantilevers. As far as we know, doping in semiconductor with selective elements offers an effective approach to adjust the electrical, optical, and magnetic properties, which is crucial for practical applications. In order to utilize the applications of nanostructure materials, it usually requires that the crystalline morphology, orientation and surface architecture of nanostructures can be well controlled during the preparation processes. In this background, the purpose of this investigation is to study the influence of Ni doping on the physical properties of ZnO thin films. Successive Ionic Layer by Adsorption and Reaction (SILAR) is an excellent method for the fabrication of undoped and doped ZnO thin films [4-7].

Experimental details

ZnO thin films were prepared using double dip technique. The 'Ni' doping was carried out by adding the respective metallic salts in the solution bath at the proportion of Zn:Ni as 100:3,5,10 respectively. ZnO thin films were grown using a two-step chemical bath deposition technique using a solution comprising 0.1 M Zinc Sulphate (99% e-Merck) , 0.2 M sodium hydroxide with a pH value of 9±0.2 deposited at bath temperature of 90 °C under optimized condition. For Ni doped ZnO (NZO) thin films $NiSO_4$ was used at a concentration of 0.1mM. Before deposition, the glass substrates were cleaned by chromic acid followed by cleaning with acetone. The well-cleaned substrates were immersed in the chemical bath for a known standardized time followed by immersion in hot water for the same time for hydrogenation. The process of solution dip (step 1) followed by hot water dipping (step 2) is repeated for known number of times. The cleaned substrate was alternatively dipped for a predetermined period in sodium zincate bath and water bath kept at room temperature and near boiling point, respectively. According to the following equation, the complex layer deposited on the substrate during the dipping in sodium zincate bath will be decomposed to ZnO due to dipping in hot water. The proposed reaction mechanism is according to the following equations [4]

$$ZnSO_4 + 2\ NaOH \rightarrow Na_2ZnO_2 + H_2SO_4 \uparrow$$
$$Na_2ZnO_2 + H_2O \rightarrow ZnO + 2\ NaOH$$

Part of the ZnO so formed was deposited onto the substrate as a strongly adherent film and the remainder formed as a precipitate. The addition of MSO_4 in the ratio of Zn:M as 100:3, 100: 10 respectively in the first dip solution leads to the formation of M doped zinc oxide nano thin films where M stands for Ni here. The ZnO thin film formed was confirmed by XRD (Rigaku Ultima III) analysis and the micro structural analysis of the samples were performed using SEM (JEOL

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Model JSM - 6390LV). The optical properties were estimated by transmittance and absorption measurements using UV-Vis NIR spectrophotometer (PerkinElmer UV WinLab 6.0.3.0730).

Table 1. Compositions and band gap values of undoped and Ni doped ZnO thin films

S.No	Solution Composition	Peak Position (A)	Energy Band Gap
1.	Ni:Zn = 0:100	382.00	3.2
2.	Ni:Zn = 3:100	382.35	3.22
3.	Ni:Zn = 5:100	382.65	3.26
4.	Ni:Zn = 10:100	379.84	3.29

RESULTS AND DISCUSSIONS

The XRD pattern of Ni doped ZnO film is shown in Figure 1. The diffraction patterns reveal good crystalline quality without any appreciable changes from pure ZnO films. These results imply that there are no secondary phases such as a Nickel or its oxides. It also shows that the high intense peak is oriented along the c-direction and the corresponding peak is (*002*). Hence, this ZnO film with stronger (*002*) preferred orientation will increase the Hall mobility [3]. The observed'd' spacing values are in good agreement with the standard values of ZnO. Hence the overall structure of the doped films remains unchanged with the introduction of Ni.

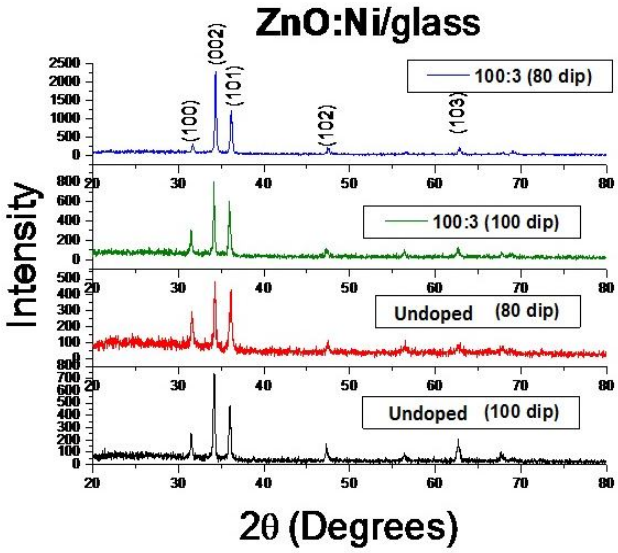

Fig. 1. The X-ray diffraction patterns for Undoped and Ni doped ZnO thin films

Also, no additional peaks of Ni or its phases are observed in the XRD spectrum (Figure 1) and it suggests that the doped Ni atoms are incorporated into the ZnO thin film. Again, the wide distribution of grain size of samples on the film can be the possible reason resulting in broadening the diffraction peaks. This may be due to the difference in ionic radii between Ni and Zn. This phenomenon in the films creates strain or stress because of mismatching Ni^{2+} in the Zn^{+2} structural and optical properties of Ni doped ZnO thin film lattice site. The Ni doping were performed under various number of dippings and concentration and the XRD patterns were obtained and are shown in Figure 1 and 2. It is observed that Ni doping shifts the peak position considerably as is shown in Figure 2 for Zn:Ni as 100:10. The typical XRD spectrum obtained for nickel doped ZnO thin films are shown in Figures 1, 2 respectively.

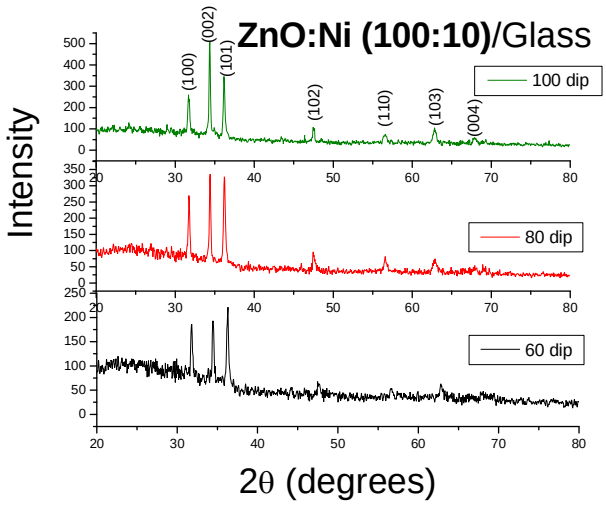

Fig. 2. The X-ray diffraction patterns for Ni doped ZnO thin films with Zn: Ni as 100: 10 in precursor solution under various number of dippings

It is observed that the increase of Ni concentration from 3 to 10 increases the intensity of the prominent peak considerably. Also the increase of thickness by increase of number of dipping also increased the intensity of the prominent peaks. The XRD pattern obtained for Zn : Ni as 100:10 showed a different behavior introducing a partial change of preferential orientation. The in addition to the intensity increase the film tend to alter the preferential orientation in 80 dip coated film . It is evident from figure 2 that the film recovers its orientation back to *(002)* surpassing *(101)*. Figure 3 shows the absorbance spectra of ZnO thin films and it revealed that the ZnO films have low absorbance in the visible region, which is a characteristic of ZnO. Also this figure shows the occurrence of peaks in the absorbance plot at arround 382 nm. These peaks are attributed to the formation of excitons in ZnO thin films, which decreased with decreasing the Ni concentration.

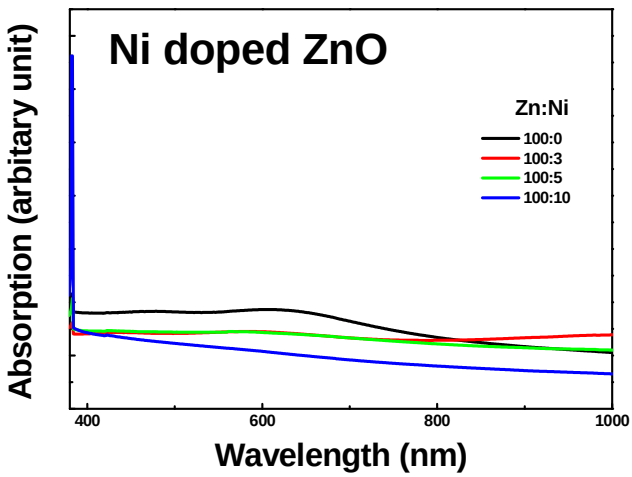

Fig. 3. The typical absorption spectra obtained for 80 dip coated Ni doped ZnO thin films with different Zn: Ni in the precursor solution

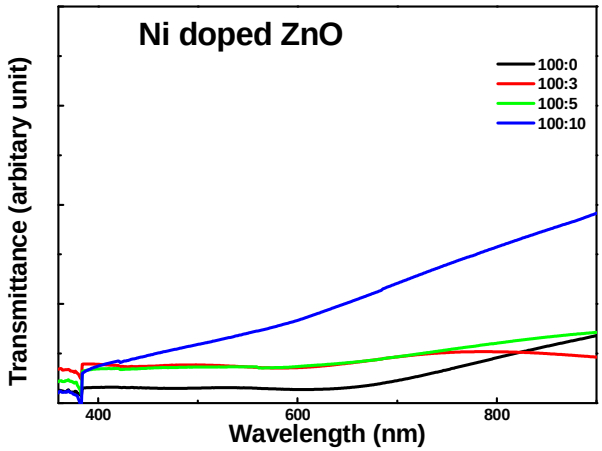

Fig. 4. The typical transmittance spectra obtained for 80 dip coated Ni doped ZnO thin films with different Zn: Ni in the precursor solution

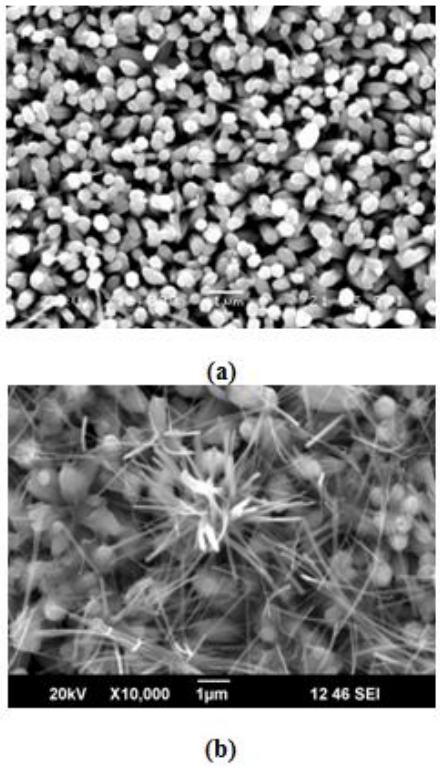

Fig. 5 (a) SEM micrograph of ZnO thin film and (b) ZnO doped with Ni.

This last parameter influences a shift between the spectra, which means a slight change of band gap energy. Figure 4 shows the transmittance spectra of ZnO thin films and it revealed that the ZnO films have low transmittance thin films in the visible region, which is also a characteristic of ZnO of very dense nanofilms. Also this figure shows the occurrence of negative peaks in the transmittance plot at arround 382 nm. The XRD studies in the same palce as that of absorption spectra. These peaks are attributed to the formation of excitons in ZnO thin films, which decreased with decreasing the Ni concentration. This bandedge influences a shift between the spectra, which means a slight change of band gap energy. Table 1 shows the band gap of the Ni doped films with Ni inclusion. The band gap energy is estimated to be around 3.2 eV. The change in the band gap value is very less attributed to Moss Burtein effect. The band gap energy slightly increases with Ni doping. The Optical properties of nickel doped ZnO thin films various Ni concentration ($NiSO_4$). The optical absorption pattern obtained in the range of 342 to 1000 nm was compared in figure 3 and the band gap variation are presented in Table 1. Figure 5 (a) shows the SEM image of ZnO thin film (un-doped) and Figure 5 (b) shows ZnO film doped with Ni. The SEM images for both un-doped and doped samples show hexagonal structure and the morphology changing with doping. Also a slight increase in the grain size is observed with Ni doping and large number of needle like randomly oriented structures also formed in the Ni doped samples. Figure 5 (a & b) shows the SEM micrographs obtained for undoped and Ni doped (Zn: Ni as 100:3) thin films. It is observed that the ZnO films can have different morphologies with varying concentration of Ni. Some features like nano needles, nanorods, nanoprisms, spindles, flower-like and hexagonal structures could be obtained by changing the SILAR parameters.

Conclusions

He XRD results shows that the overall structure of the doped films remain unchanged with the introduction of Ni. Also, no additional peaks of Ni or its phases are observed in the XRD spectrum and it suggests that the doped Ni atoms are incorporated into the ZnO thin film. SEM micrographs revealed ZnO films can be takes many shapes: nano needles and hexagonal structures. The ZnO films with (*002*) texturing is observed due to Ni doping and hence the newly developed material is also a promising candidate for solar cells, photo detectors and thin film gas sensing. The band gap increases with Ni doping slightly and is attributed to Moss Burstein effect. The Morphological varaiations are also reported.

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