

Morphological and optical properties of sol-gel derived Ni doped ZnO thin film

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Abstract

In this work, we are interested in thin films of zinc oxide doped with nickel (Ni), deposited on glass substrates and elaborated by the sol-gel dip coating technique. The effects of the doping concentration in the range of outlet (1%, 3% and 5at%) have been thoroughly studied. The morphological properties of ZnO-Ni films were studied by Atomic Force Microscopy (AFM). The optical properties of the ZnO:Ni thin films were examined by UV-visible spectroscopy and the Tauc method was used to estimate the optical band gap and hall effect for electrical characteristic. Atomic Force Microscopy has indicated that the surface of the ZnO:Ni thin films have uniform and dense ZnO grains. The optical transmittance of ZnO:Ni thin films increased from 86 to about 93% from pure ZnO films to ZnO film doped with 3 wt% Ni and then decreased for 5 wt% Ni, and the optical band gap from 3.297 eV to 3.23eV. The electrical characterization performed using the technique of hall effect, gave a maximum electrical conductivity of $9.3 \cdot 10^3 (\Omega \cdot \text{cm})^{-1}$ obtained for the film doped with 3%Ni.

Keywords: Ni doped ZnO, Thin films ZnO, Optical properties, Sol gel method, dip coating.

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1. Introduction

In recent years, thin films of zinc oxide have acquired an increasing interest in many research fields because of its many potential applications. The zinc oxide thin film can be used as a very sensitive sensor in chemical gas sensors, as pressure sensor or in electronic devices such as rectifiers, filters, resonators and for radio communications in the manufacture of varistors. Many deposition techniques were used for the production of ZnO thin films, such as laser ablation [1], spray pyrolysis [2], rf-magnetron sputtering [3], CVD [4], molecular beam epitaxy[5],vapor-liquid-solid (VLC) method [6] and the process sol gel [7,8] etc. In this paper, thin films of ZnO:Ni were deposited by the sol gel method associated to the dip coating technique using a solution of zinc acetate aim of glass substrates. The objective in this work is to study the effect of

nickel doping level by Nickel on the morphological, optical and electrical properties of ZnO:Ni thin films.

2. Experimental part:

2-Methoxyethanol and monoethanolamine (MEA) are used as the solvent and stabilizing agent, respectively. Dihydrate Zinc acetate $[\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}]$ and dihydrate nickel acetate $[\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}]$ are dissolved in a mixture of 2-Methoxyethanol and monoethanolamine at room temperature. The concentration of zinc acetate is 0.1 M and the molar ratio of MEA to Zn is maintained at 1.0. ZnO precursor containing Ni-dopants were prepared with different percents (1, 3 and 5at %). The resulting mixture solution was stirred for 3h at 65°C to yield a clear and homogenous solution. The films ZnO:Ni were prepared by dip-coating method at controlled withdrawal speed 50 mm min⁻¹. Each coated

layer was dried at 200°C for 10 min-1, and the films were annealed at 500°C for 2 hours in air.

The surface morphology was observed by atomic force microscope (AFM). The optical properties have been studied by a spectrophotometer and the conductivity of the ZnO:Ni thin films were measured by the Hall Effect technique.

3. Results

3.1. Surface morphology

Fig. 1 shows the AFM micrographs of the surface profile for ZnO :Ni thin films. The Films of pure ZnO and ZnO doped with Ni at different concentration deferens show that the surface is uniform, which contains spherical grains of various sizes. The calculated size of the grains of ZnO films. Neither is given in Table 1 As can be seen, the grain size increases with the concentration of Ni, it goes from 42 nm to 85 nm for pure ZnO and doped ZnO 5at% Ni respectively.

3.2. Optical properties

The optical properties of thin films of ZnO:Ni was determined from the transmission measurement in the range of 300-1100 nm. Figure 2 shows the optical transmission spectra of ZnO:Ni films prepared with different doping levels in Ni. All films show a high transmittance in the UV region of the order of 86-93%. It was observed that the transmittance increases with the increase of Nickel concentration with a maximum value obtained at 3% Nickel. Beyond 5% the transmittance decreases with the increase of the Ni dopant concentration. The transmittance increased to 3 wt% of Ni because the pure ZnO films are porous. Due to doping, nickel atoms occupy vacant sites in ZnO and reduce the dispersion of light and therefore the transmission factor increases with the increase of doping up to 3% of Ni. With an additional increase in the concentration of doping, nickel atoms occupy interstitial sites in the ZnO and increase the absorption of light, and therefore a decrease in transmittance.

The optical energy gap of pure ZnO thin films doped with different rate of nickel doping is given by the following equation [9]:

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

Where A is a constant and E_g is the gap energy. The value of the gap energy can be determined from the intersection of the curve $(\alpha h\nu)^{1/2} = f(h\nu)$ with the axis of

abscissas [10,11] as is shown in Figure 3. absorption Coefficient α can be calculated from the transmittance of ZnO:Ni film with the formula $\alpha = (1/d) \ln (1/T)$, where d: thickness of films ZnO:Ni and T: the value of transmission. The evolution of the optical gap of the films according to doping is reported in Figure 4.

It can be seen that the optical band gap energy of undoped ZnO film is 3.247 eV. The effect of the Ni doping on films has increased the E_g values from 3.247 to 3.267 and 3.297 eV for 1 and 3 wt% doped films, respectively. Blue shift due to Ni doping has been largely ascribed to the Burstein-Moss effect. DiTrollo et al. have reported a large variation of E_g of ZnO film with increasing Ni doping concentration [12].

3.3. Electrical properties

Figure 5 shows the evolution of the conductivity of the films of ZnO:Ni as a function of the dopant concentration (Ni). This curve shows that the conductivity of the ZnO thin film: Ni increases with the increase of the dopant concentration of Ni and reaches its maximum value of $9.310^3 (\Omega \cdot \text{cm})^{-1}$ doping for 3wt% Ni, then it decreases to $4.210^3 (\Omega \cdot \text{cm})^{-1}$. This increase in conductivity with increasing concentration of doping can be performed by increasing the number of charge carriers (electrons) from the donor ions Ni^{2+} incorporated in substitutional or interstitial sites of Zn^{2+} cation [14]. The reduction of conductivity beyond 3wt% Ni may be due to a decrease in the carrier mobility due to excessive Ni.

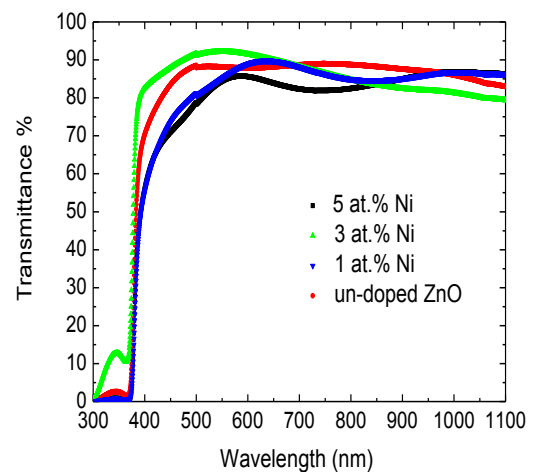


Fig. 2. Transmittance spectra of ZnO:Ni thin films with various Ni doping contents.

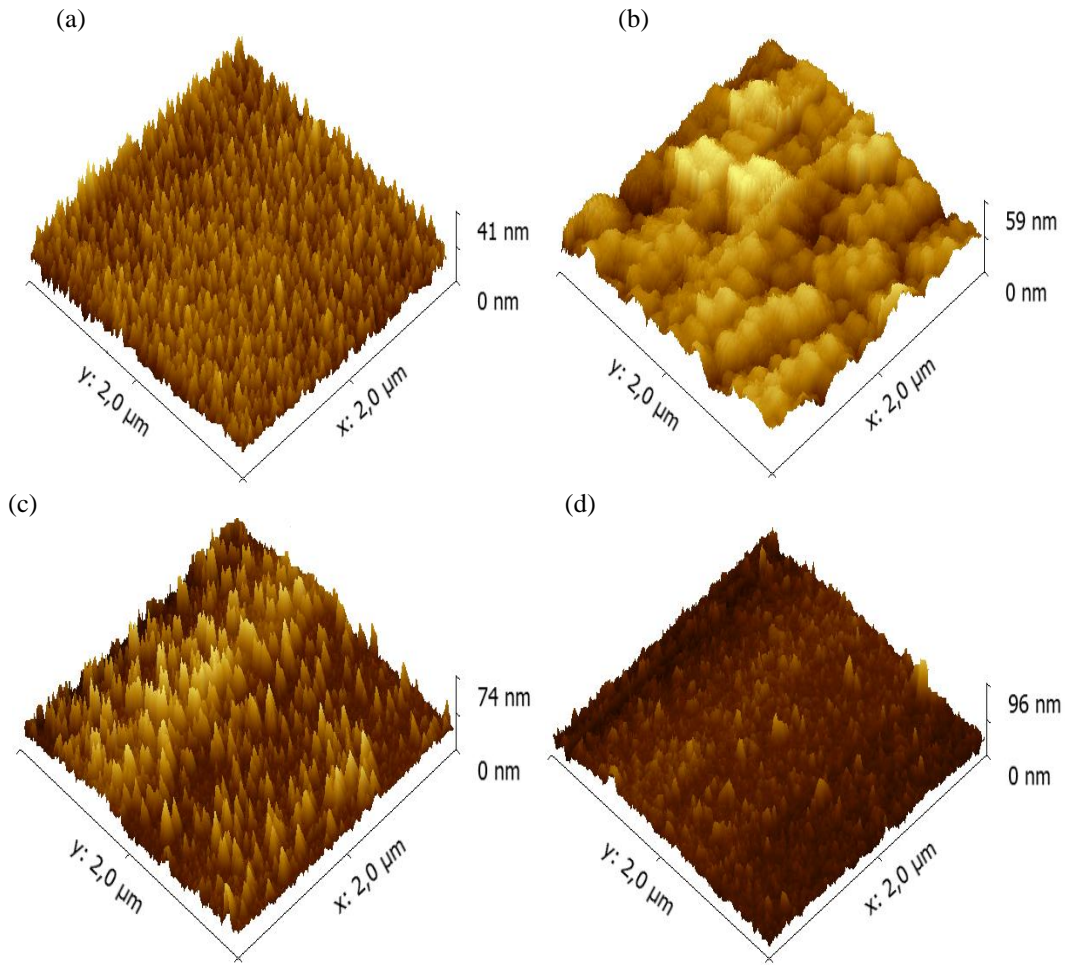


Fig. 1. Three dimensional AFM images of ZnO :Ni thin films at different concentration (a) 0%, (b) 1%, (c) 3% and (d) 5 %

Table 1 Average grain size of the Ni:ZnO thin films with different Ni doping contents.

Samples	Average crystallite size (nm)
Ni content at%	
0	42
1	59
3	71
5	85

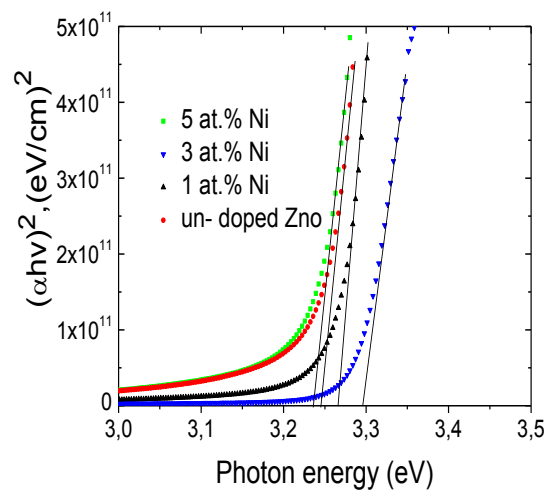


Fig. 3.Plot of $(\alpha hv)^2$ versus $h\nu$ curves of ZnO :Ni thin films.

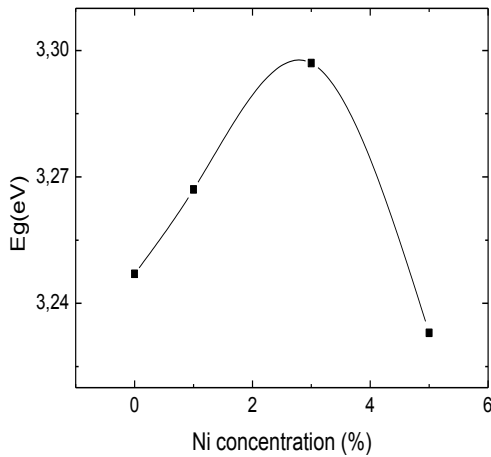


Fig. 4. The optical band gap as a function of Ni doping concentration.

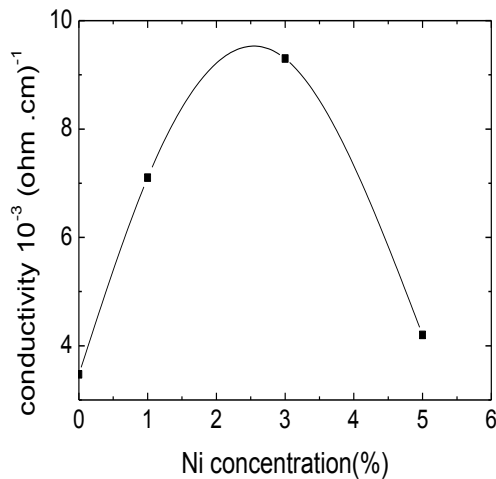


Fig. 5. Electrical conductivity of ZnO :Ni thin films

5. Conclusion

In this work, we have developed and characterised thin films of ZnO doped with pure nickel by sol-gel on glass substrates. The atomic force microscope shows spherical grains of different sizes. The ZnO film:Ni developed showed high transmittance which is greater than 86% in the visible region and the optical gap increases with increasing the concentration of Ni. Furthermore, it was found the increase in conductivity with increasing the concentration of Ni up to 9.3×10^{-3} ($\Omega \cdot \text{cm}$)⁻¹ and has a maximum value obtained for films doped 3% Ni.

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