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The effect of Cu-doping on physical properties of nanostructured NiO thin films prepared by spray pyrolysis technique

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KEYWORDS
NiO;
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Abstract. Undoped and copper doped nickel oxide films, prepared onto glass substrate by spray pyrolysis method, were studied from various physical view points including: morphological, structural, optical, electrical and thermo-electrical properties. The XRD patterns show that the nano-sized grains have cubic polycrystalline nature (with no additional related Cu-content phase), and the data analysis revealed while the crystallite sizes are decreased (13-10.5 nm) the dislocation density is increased ($5.92 \times 10^{-3} - 9.07 \times 10^{-3}$ nm^{-2}) with increments in the doping density. The electrical and thermo-electrical data (Seebeck effect) confirmed more substitutions of Cu^{+} ions with Ni^{2+} ions and in turn more p-type conductivity in samples with higher doping. Optical measurements showed that the direct and indirect band gaps of the transparent conductive layers are decreased. These variations are in good agreement with the variations of the crystallite sizes and carrier densities of the samples.

1. Introduction

In recent years there has been a great interest in the investigation of nano crystalline nickel oxide films. Nickel oxide is a wide band gap, low cost, promising ion storage material in terms of cyclic stability; undoped NiO has a wide direct band gap of 3.5-4 eV and exhibits low p-type conductivity as a result of the presence of intrinsic crystal defects, mainly Ni^{2+} vacancies in the lattice [1-3]; otherwise, if NiO has perfect stoichiometric, so it is a Mott-Hubbard insulator with a resistivity of the order of 10^{13} Ω.cm at room temperature [4]. The goal behind doping in such layers is to control the resistivity of a sample to a desired value by changing its content, intentionally. Many researchers have tried to investigate the effect of various doping elements such as Li, Al, Fe on physical properties of NiO thin layers using various methods [2,5-7]. They have found that the surface morphology, crystal composition, uniformity and the physical properties of the films like resistivity and transparency etc. depend on the nature and amount of dopant. As far as the Cu doped NiO film is concerned, very few studies have been reported in the literature. It would, therefore, be interesting to investigate the Cu doped NiO films by using the low cost spray pyrolysis technique. NiO films have been prepared by variety of physical and chemical techniques, such as sputtering, Pulsed Laser Deposition (PLD), Chemical Vapour Deposition (CVD), electron beam evaporation, sol-gel, and spray pyrolysis technique. The nickel oxide has excellent chemical stability, optical and electrical properties so it was used for chemical sensors, gas sensor, dye-sensitised solar cell and smart windows [4-10].

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2. Materials and method

Nickel oxide thin films have been deposited from 0.1 M aqueous solution of nickel chloride $NiCl_2.6H_2O$ by spray pyrolysis technique onto glass substrates. For copper doping $CuCl_2.H_2O$ powder was dissolved in precursor solution of $NiCl_2$ with different weight percentages (W.%). The Cu-doped films were prepared with various (0, 1, 5, and 10 W.%) copper concentrations. The NiO films were deposited with the same conditions of: solution volume 50 ml, deposition rate 5 ml/min, nozzle to substrate distance 35 cm, and the optimized substrate temperature of 350°C. The surface morphology was studied using Hitachi S-4160 Scanning Electron Microscope (SEM); the structural characterization was carried out by D8 Advance-Bruker diffractometer with Cu K_α radiation ($\lambda = 1.54$ Å). The transmittance and reflectance spectra of films were recorded using UV-Vis. (300-1100 nm) spectrophotometer, Shimadzo-1800. For I-V measurement an electrochemical analysis system (BHP20634) was used. Also profilemeter Taylor/Hobson was used for measuring the thickness of the layers.

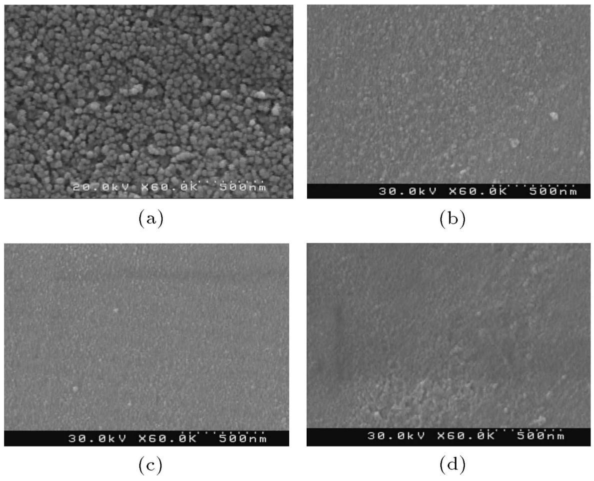
3. Results and discussion

3.1. Morphological characterization

The SEM images of NiO films are shown in Figure 1. As it is clear, in undoped sample (Figure 1(a)), it is uniformly covered by nano-scale grains with an average diameter of $\sim$ 40 nm. According to other images, in doped films (Figure 1(b)-(d)), the surface of the layers become smoother as the doping concentration is increased.

3.2. Structural properties

The XRD patterns of thin layers are shown in Figure 2.



(a) (b)

(c) (d)

Figure 1. The SEM images of un-doped and different doping percentages of copper: (a) 0 W%; (b) 1 W%; (c) 5 W%; and (d) 10 W%.

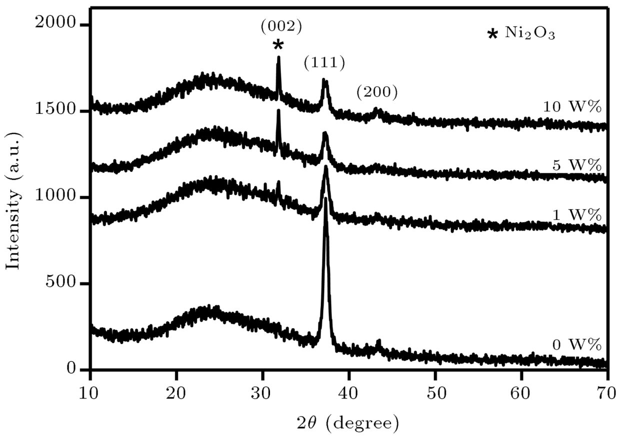


Figure 2. The XRD patterns for various Cu-doped NiO thin films.

Table 1. The crystalline size (D), strain (ε) and dislocation density (δ) of the studied layers.

Cu-content W%	***D* (nm)**	**ε ($\times 10^{-3}$)**	**δ ($\times 10^{-3}$nm^{-2})**
0	13.00	2.67	5.92
1	12.95	2.67	5.96
5	12.83	2.72	6.08
10	10.50	3.31	9.07

As is clear, while the preferred cubic NiO crystalline direction in undoped sample, i.e. (111), is decreased, as the doping concentration has increased, an additional nickel oxide crystalline phase of Ni_2O_3 with hexagonal structure along (002) direction is formed around Bragg diffraction angle of 31 degree. It is notable that no additional phase with Cu content is appeared in doped samples. According to the main NiO phase data analysis (Eqs. (1)-(3)), a number of structural parameters including: crystallite size (D), induced strain (ε) and line dislocation density (δ) have been calculated [8]. The results are noted in Table 1.

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \tag{1}$$

$$\varepsilon = \frac{\beta \cos\theta}{4}, \tag{2}$$

$$\delta = \frac{1}{D^2}, \tag{3}$$

where λ is the X-ray wavelength, β is the Full Width at Half Maximum (FWHM) of preferred (111) direction, and θ is the Bragg angle.

As is evident, although increments in the doping density tend to decrease the crystallite size (from 13 to 10.5 nm), the amount of the induced strains and especially the dislocation densities, which lead to creation of defect levels in the band gap, are raised. These results are compatible with the difference in the ion sizes of the substituted Cu^{+} ions (0.96 Å) with that of the Ni^{2+} ions (0.78 Å) [9]. These variations are quite effective on electrical and optical properties of the layers, as discussed in the following.

3.3. Electrical and thermo-electrical measurements

Figure 3 shows the I-V characteristics of undoped and doped samples. According to these results it is apparent that the sheet resistance of the layers is decreased substantially from 240 to 52.2 M$\Omega/\Box$ (or resistivity changes from ~ 5 to 1 kΩ.cm) as the Cu-doping concentration is increased with the lowest in sample with highest doping density of 10 W.%. This could be attributed to the fact that Ni^{2+} ions in the NiO lattice are replaced by Cu^{+} ions, that in turn lead to more acceptor levels close the valence band edge and therefore more electrical conduction [10]. Seebeck experiment data (Figure 4) and the positive sign for Seebeck coefficient (S) in Eq. (4) confirmed that all layers have p-type conduction.

$$V = S\delta T, \tag{4}$$

where V is thermoelectromotive force, and δT is the temperature difference between two ends.

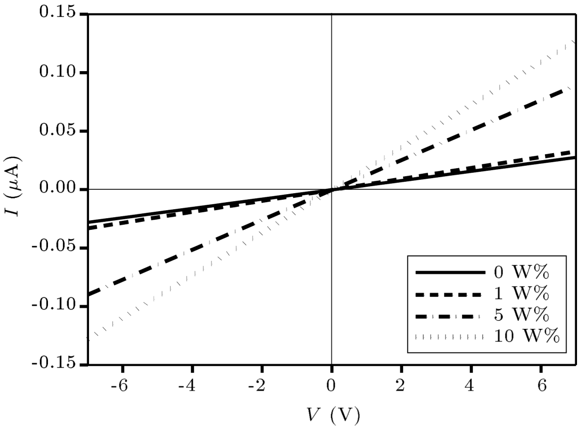


Figure 3. The I-V characteristics of NiO:Cu films with various copper concentrations.

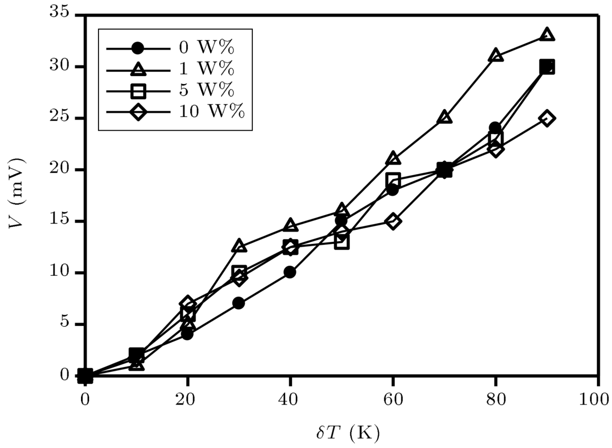


Figure 4. The variation of thermoelectric power vs. temperature difference in NiO:Cu films.

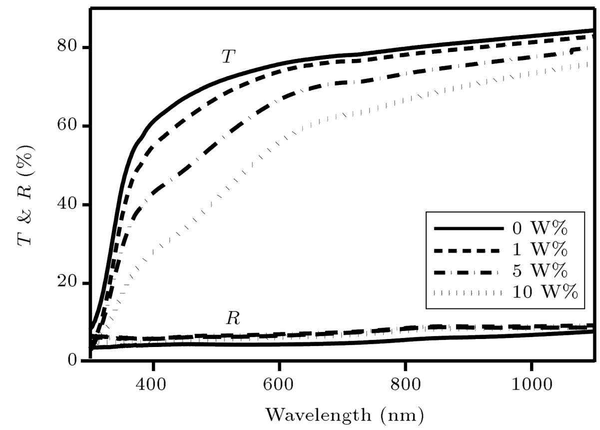


Figure 5. The transmittance and reflectance spectra in the studied samples.

3.4. Optical properties

The variations in transmittance and reflectance of NiO:Cu thin films are shown in Figure 5. It is notable that the variations of transmittance of the films are consistent with the variations of crystallite size of the layers Table 1; the smaller crystallite sizes, the lower optical transmittance of the films as a result of higher photon scattering by the crystallite boundaries [11]. The descending and ascending behaviours of transmittance and reflectance spectra, respectively, are consistent with the rise in conductivity of the layers and therefore the relative metallic-like properties of the layers. It is known that the presence of free carriers is among the most effective parameters of light absorption at long wavelength in thin semiconductor layers [12].

The wavelength dependent absorption coefficients, α_λ, of the films are calculated using the formula [11]:

$$\alpha_\lambda = \frac{1}{d} \ln \left(\frac{(1 - R_\lambda)^2}{T_\lambda} \right), \tag{5}$$

where d is the thickness of the layer (~ 220 ± 20 nm), also T_λ and R_λ are related to the transmittance and reflectance spectra of the layers. Using these data, we found the optical band gap, E_g, of the studied films by [2]:

$$(\alpha_\lambda hv)^m = A(hv - E_g), \tag{6}$$

where A is constant, hv is the incident photon energy, and m depends on the nature of band transition ($m = 2$ for direct transitions and $m = 1/2$ for indirect ones). The results are shown in Figure 6. The extrapolation of the data in the linear-high photon energy region with the energy axis, i.e. $\alpha_\lambda hv = 0$, gives the direct and indirect values of the optical band gaps of the

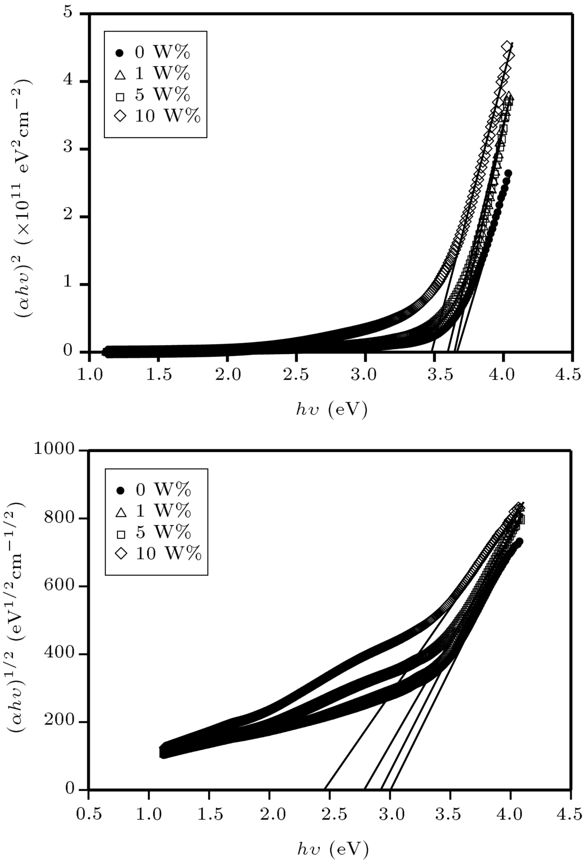


Figure 6. Plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for various Cu-doped NiO thin films.

layers. According to these analyses we found the direct band gap (E_{gd}) varies from 3.66 eV to 3.46 eV and the indirect one, E_{gind}, changes from 3 to 2.45 eV as the doping concentration increases. According to these results, in spite of nanoscale grains and crystallites, the reduction in direct and indirect band gaps could be due to the formation of band tails as a result of Cu impurities and also defect levels close to the valence band edge. As it is known, the wider the band tail in a material, a smaller optical band gap is expected.

4. Conclusions

In this paper, we reported the effect of Cu-doping (0, 1, 5, 10 W.%) in NiO thin films which are prepared on glass substrates by spray pyrolysis method. Samples were characterised by morphological, structural, electrical, thermo-electrical, and optical properties. The SEM images of the layers showed although in undoped layer it is uniformly covered by nano-scale grains ($\sim$ 40 nm), in doped ones the particles are gradually disappeared and the surface of the layers become smoother. The XRD patterns showed all the films have cubic structure with preferred orientation (111) direction plus Ni_2O_3 phase as Cu atoms are added. Seebeck effect experiment indicated that all films have p-type conductivity and the I-V data revealed that the resistivities of the layers are decreased with increasing Cu concentration. Finally UV-Vis. spectra showed that in visible region, the transmittance of the films are decreased from 70% to 50% with increasing Cu-doping, as the result of decreasing the crystallite size and increasing the hole density in the layers.

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