STUDY THE EFFECT OF Cu DOPING ON OPTICAL AND STRUCTURAL PROPERTIES OF NiO THIN FILMS

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Article Info	Abstract
<p><i>Received:</i> 10.01.2020 <i>Accepted:</i> 07.04.2020</p> <p>Keywords: Cu, NiO, Thin films, Spin coater method, polycrystalline structure, Electrical conductivity.</p>	<p>In this work, copper doped nickel oxide as the thin films have been elaborated by a spin coating method, the nickel chloride hexahydrate (0.8M) and copper (II) chloride dehydrate (Cu/Ni = 0, 2.15, 4.3, 8.6 and 12.9 At.%) were used to prepare the Cu doped NiO thin films. The Cu doped NiO thin films were heated at a crystallization temperature of 600 °C with 2 h. The obtained thin films by spin coater method have a film thickness in the order of 400 nm. The prepared Cu doped NiO thin films have a polycrystalline with cubic structure (200) peak was observed. The optical property shows that the prepared thin films have a transmittance of about 70 %. The Cu doped NiO thin films have minimum bandgap energy is 3.85 eV at 12.9 at.%, the thin film deposited at 8.6 at.% has the highest value of Urbach energy is 425 meV. The Cu doped NiO thin films have a high electrical conductivity of 8.6 at% it is $7 (\Omega \cdot \text{cm})^{-1}$. The prepared Cu doped NiO thin film was suitable for gas sensing applications due to the existing phase and higher electrical conductivity.</p>

1. Introduction

In the latest research, for the important subjects, in the field of materials science, the synthesis of thin films from a metal oxide (semiconductor) that was used as a gas sensor. The Nickel oxide was found a belongs to a class of the semiconductor materials, it was found in the cubic structure, and has a good transparent in the thin film. NiO was used in sciences and technology as the optoelectronic field due to the good structure crystallinity and the best transmittance was obtained at the longer wavelength smaller than the 400 nm. The bandgap energy of NiO thin films varied between 3.6 to 4 eV. However, the thin films of NiO can be used in various applications due to the simplicity of synthesis such as solar cells, chemical

sensors, photodetectors, electrochromic mirrors, organic light-emitting diodes, UV detectors, smart windows, and defrosting windows [1-6].

The thin films of NiO can be obtained by various deposition methods likely electrochemical deposition, pulsed laser deposition, magnetron sputtering, molecular beam epitaxy (MBE), reactive evaporation, sol-gel process, chemical vapor deposition, and spray pyrolysis [7-9]. NiO has been intensively studied as a promising material for gas sensors in the detection due to the range of wide bandgap (3.6–4.0 eV) and high stability that are similar to ZnO [10,11].

The aim of this work is to obtain a thin film with good physical properties for gas sensing applications, which can be obtained through the largest absorption values, and this indicates a decrease in the optical band gap energy. In the past research, the literature was investigated the NiO thin film as detection in the environment for various gases such as CO, CO₂, SO₂, NO₂, CH₄. However, we have prepared the Cu doped NiO thin films for further application in gas sensing due to the incorporation of the Cu with Ni in increasing the electrical conductivity. The spin coating method has been used in this work to fabricate the thin films of Cu doped NiO, these thin films were fabricated on a substrate of microscope glass. The films were prepared with 0.8 M at a crystallization temperature of 600 °C. The influence of Cu concentration on optical, structural and electrical characterizations of Cu doped NiO has been studied.

2. Experiments

2.1. Solution preparation

The prepared solutions Cu doped NiO have been dissolved of 0.8 M of the nickel chloride hexahydrate NiCl₂·6H₂O in the absolute H₂O, HCl was used as a stabilization solution of NiO, and the copper(II) chloride dihydrate CuCl₂·2H₂O was used to prepare the CuO solution. The final mixture solution of (Cu/Ni) = 0, 2.15, 4.3, 8.6 and 12.9 At.% were stirred and heated at 40 °C to have a solution with high transparency. The film coating was deposited two days after the preparation.

2.2. Thin films preparation

The Cu doped NiO samples have been elaborated by dropping the Cu doped NiO solution on a glass substrate at room temperature by a spin coating method, which has been the speed of rotating confined between 2500 to 3000 rpm for 45s, which it is repeated 20 times. The Cu doped NiO thin films have been elaborated at several Cu concentrations are 0,

2.15, 4.3, 8.6 and 12.9 At.%. The thin films become heated at a temperature of 200 °C, and then annealed for the crystallization of the Cu doped NiO thin films at 600 °C in air for 2 h. Table 1 shows the experimental conditions such as the concentration of Cu, deposition rate, deposition time, the annealing temperature and the final measured film thickness of Cu doped NiO thin films. The final Cu doped NiO thin films were stayed for one to three weeks after deposition to characterize.

Table 1. The experimental conditions of deposition Cu doped NiO by spin coating method.

Sample number	Cu concentrations (At.%)	Deposition rate (ml)	Deposition time (s)	Annealing temperature (°C)	Final film thickness (nm)
1	0	3	45	600	390
2	2.15	3	45	600	450
3	4.3	3	45	600	420
4	8.6	3	45	600	430
5	12.9	3	45	600	380

2.3. Thin films characterization

The Cu doped NiO thin films have been characterized in order to get the physical properties such as optical, structural and electrical. The optical transmittance of fabricated Cu doped NiO films was measured by a UV-visible (35-LAMBDA) in the range of 300–1000 nm. The crystalline structure of fabricated films were obtained by X-ray diffraction (Bruker-XRD AXS-8D, $\lambda_{\text{CuK}\alpha} = 0.15406$ nm with 2θ varying between 30° and 50°). And the electrical conductivity was measured by injection current-voltage by four-point method into the deposited film surface. All characterizations have been made at stable conditions.

3. Results and discussion

In Fig. 1, the variation of optical transmittance of elaborated Cu doped NiO thin films have been presented as a function of the longer of the wavelength in the range of 300–1000 nm. As seen from these spectra's the transmittance of Cu doped NiO thin films were decreased with increasing Cu concentration in the visible region, the maximum transmittance of Cu doped NiO thin films were obtained for 0, 2.15 and 4.3 at.%, it is 70% caused by the interstitial site of Cu and Ni. The transmission of Cu doped NiO thin films at higher

concentrations in the visible region was decreased due to the increase in absorption. When the absorption condition was satisfied, the detection was beginning and the gas concentration, which was comparable at a higher concentration of Cu. The band gap energy of fabricated thin films of Cu doped NiO have been derived from the direct transitions of inter-band in the valence band and conduction band, it was determined by following equation [12]:

Figure 1. The variation of optical transmittance (T) as a function of longer of the wavelength (λ) of fabricated Cu doped NiO thin film deposited at several Cu concentrations.

$$(Ah\nu)^2 = B(h\nu - E_g) \quad (1)$$

where A , $h\nu$, C and E_g are the absorbance, the energy of the photon, a constant and the band gap energy of Cu doped NiO thin films, respectively. However, the tail width can be calculated using the Urbach energy for the absorption coefficient at lower photon energy [13]:

$$A = A_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (2)$$

where A , $h\nu$, A_0 and E_u are the absorbance, the energy of the photon, a constant and the Urbach energy, respectively. The Urbach energy has been determined by deducing the curves of the variation of $\ln A$ with the photon energy $h\nu$ to obtain of Urbach energy values of Cu doped NiO thin films.

Fig. 2 shows the variation of the band gap energy and the Urbach energy of fabricated Cu doped NiO thin films at several Cu concentrations. As seen, the band gap energy

decreased with increasing of Cu concentration to the highest value of 3.85 eV was obtained with 12.9 at.%Cu (see Table 2), this decrease can be explained by the corporation between Ni and Cu in the interstitial site, which was showed for the oxygen vacancy. However, the Urbach energy was increased from 325 meV for 0 at.% to 425 meV for 8.6 at.% (see Table 2), and then decreased to 395 meV for 12.9 at.%, the decrease of Urbach energy of Cu doped NiO thin films can be linked by the decrease of the defects in the film network and the increase can be related the reduction of absorption, which is shown for the higher transmittance of fabricated Cu doped NiO thin films for the lowest concentration.

Figure 2. The variation of bandgap energy and Urbach energy of fabricated Cu doped NiO thin films at several Cu concentrations.

Table 2. The variation of the band gap energy and the Urbach energy of Cu doped NiO thin films at different Cu concentrations.

Cu concentration (at.%)	Optical band gap energy E_g (eV)	Urbach energy E_u (meV)	Film thickness d (nm)
0	3.98	325	390
2.15	3.97	355	450
4.3	3.92	380	420
8.6	3.89	425	430
12.9	3.85	395	380

The crystalline structure of Cu doped NiO thin films is detected in Fig. 3, it is presented the X-ray diffraction variation in the range of $2\theta = 30^\circ$ to 50° . The NiO thin film prepared at

0 at% Cu presented two diffraction peaks were (111) and (200) peak. After doping, we have observed only one diffraction peak at $2\theta = 43.5^\circ$, it is (200) peak of NiO cubic structure in nature, which it fined that the elaborated Cu doped NiO thin films have a polycrystalline structure with (200) plan. This attribution was detected that the Cu doped NiO thin films have been preferred to (200) plan. This material was suitable for gas sensing applications due to the existing phase and can change the transfer of the free electron.

Figure. 3. XRD spectra of fabricated thin films of Cu doped NiO deposited at several Cu concentrations.

The electrical conductivity σ of Cu doped NiO thin films was determined by four-points probe method, it is based on measured the sheet resistance R_{sh} of the films as expressed by:

$$R_{sh} = \frac{\pi}{\ln(2)} \cdot \frac{V}{I} \quad (3)$$

$$\sigma = \frac{I}{\rho} = \frac{1}{dR_{sh}} \quad (4)$$

where ρ is the electrical resistivity, d is the film thickness, I is the applied current = 1 nA and V is the measurement voltage (see Table 3).

The electrical conductivity of fabricated Cu doped NiO thin films is placed in Fig. 4 and Table 3, as seen, the electrical conductivity was increased from $2.1 (\Omega \cdot \text{cm})^{-1}$ for 0 at.% to $7 (\Omega \cdot \text{cm})^{-1}$ for 8.6 at.% (see Table 1), and then decreased to $3.5 (\Omega \cdot \text{cm})^{-1}$ for 12.9 at.%, it is

comparable with the variation of tail energy (see Fig. 2). The decrease of electrical conductivity of Cu doped NiO thin films caused by the oxygen vacancy and the increase can be linked by the oxygen diffusion. The increase of electrical conductivity of Cu doped NiO thin films can be to the increases sensor time of gas detection.

Table 3. The electrical characterizations of Cu doped NiO thin films at different Cu concentrations.

Cu concentration (at.%)	Sheet resistance R_{sh} (Ω)	Electrical conductivity σ ($\Omega.cm$) ⁻¹	Film thickness d (nm)
0	12210.2	2.1	390
2.15	6944.4	3.2	450
4.3	5291.1	4.5	420
8.6	3322.2	7	430
12.9	7518.8	3.5	380

^a. Optical band gap energy

^b. Urbach energy

^c. Film thickness

Figure 4. The electrical conductivity of fabricated Cu doped NiO thin films at different Cu concentrations.

4. Conclusions

In this work, nickel oxide doping with copper (Cu doped NiO), where (Cu/Ni) = 0, 2.15, 4.3, 8.6 and 12.9 At.% were successfully elaborated on a glass substrate by spin coating method with 0.8 M using nickel chloride hexahydrate and the ration of copper(II) chloride dehydrate. The Cu doped NiO thin films have been heated at a crystallization temperature of 600 °C for 2 h. The obtained thin films by spin coater method have a film thickness in the

order of 400 nm. Cu doped NiO thin films were observed a polycrystalline a cubic structure (200) peak was observed. All prepared thin films have an average transmittance is approx. 70 % in the region of visible. The decrease in the transmission of Cu doped NiO thin films at a higher concentration due to the increase in absorption, which it indicated to begin the gas detection such as the example of our work. The Cu doped NiO thin films have minimum band gap energy is 3.85 eV at 12.9 at.%, the thin film deposited at 8.6 at.% has the highest value of Urbach energy is 425 meV. The Cu doped NiO thin films prepared 8.6 at% has the highest electrical conductivity is $7 (\Omega.\text{cm})^{-1}$. The increase of electrical conductivity of Cu doped NiO thin films can be to the increases sensor time of gas detection. The prepared Cu doped NiO thin film was suitable for gas sensing applications due to the existing phase and higher electrical conductivity.

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