

The Effect of Ni Dopant on the Structural and Optical Properties of CdO Thin Films Deposited by Spray Pyrolysis Method

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Abstract: In this work the effect of Ni dopant on structural and optical properties of cadmium oxides, CdO, semiconductor films had been studied, which prepared with 300 nm thickness by spray pyrolysis method at 250°C substrate temperatures on glass substrates from 0.1M cadmium chloride dissolved in distilled water. The structural properties were studied by X-ray diffraction analysis , while the optical properties were studied by UV- visible spectroscopy.

Keywords: CdO thin film, spray pyrolysis, structural properties, optical properties.

I. INTRODUCTION

Cadmium oxide (CdO) is an II-VI compound n-type semiconductor with a simple cubic structure having a direct band gap of 2.3 eV [1]. Its high electrical conductivity and high optical transmittance in the visible region of solar spectrum [2] which has found extensive applications in solar cells [3].

There are variety of deposition techniques reported to obtain CdO films, such as sol-gel technique [4], pulsed laser deposition [5], chemical bath deposition [6], and spray pyrolysis [7]. The chemical spray pyrolysis method is the simplest, lowest cost, and suitable for deposition onto large area. It was observed that when the size of the dopant ion is slightly smaller than that of Cd²⁺ ion, then the conductivity, mobility and carrier concentration of CdO are improved and the lattice unit cell compresses.[8, 9]. This study focused on the effect of Ni dopant on structural and optical properties of cadmium oxides, CdO, semiconductor films, which prepared by spray pyrolysis method at 250°C substrate temperatures on glass substrates.

II. EXPERIMENTAL PROCEDURE

Pure and doped cadmium oxides films with nickel have been produced by spraying aqueous solution of (0.1) M of cadmium chloride with (0, 2 and 4) % nickel chloride dissolved in distilled water onto glass substrates (1x25x75mm³) at 250°C substrate temperature. The substrate temperature was maintained to within $\pm 5^\circ\text{C}$. 50 ml. The used cadmium chloride and nickel chloride mass was calculated using the following equation:

$Weight (g) = Molarity (mol/l) * Volume (l) * Molecular weight (g/mol) \dots \dots \dots I$

Prior to deposition, the substrates were cleaned with cleaner solution, distilled water and followed by alcohol using ultrasonic bath.

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The spray pyrolysis is basically a chemical process, that is the spraying of the solution onto a substrate held at high temperature, where the solution reacts forming the desired film. The spray rate of the solution was adjusted to be five sprinkling in minute, the sprinkling time about ten second. The normalized distance between the spray nozzle and the substrate is 30cm. Compressed air was used as the carrier gas. The temperature of the substrate was controlled by an Iron-Constantan thermocouple. The thickness of the films (t) was determined using Michelson interferometer. X-ray diffraction (XRD) pattern of the deposited films on corning glass substrate were examined by SHIMADZU XRD-6000 X-ray diffractometer (Cu_{Kα} radiation λ=0.154nm) in 2θ range from 20° to 80°. Optical transmittance spectrum was recorded, at room temperature, in the wavelength range 300-1100nm using OPTIMA SP-3000 UV-VIS spectrophotometer.

III. RESULTS AND DISCUSSION

Fig. (1) shows XRD for 300 nm pure and doped CdO thin film deposited on glass, it shows that all films have a polycrystalline structure with five peaks for (CdO) located at 2θ=32.786, 38.076, 55.126, 65.786 and 69.126° with hkl (111), (200), (220), (311) and (222) respectively with a good identically with standard peaks. It is obvious that the doping with Ni helps to improve the crystalline quality of the CdO thin films.

The interplaner distanced d_{hkl} for different planes are measured using Bragg law [10]:

$$2d \sin \theta = m \lambda \quad \dots\dots\dots 2$$

while the average crystallite size estimated by Scherrer's formula [10]:

$$b = \frac{0.89 \lambda}{\Delta(2\theta) \cdot \cos(\theta)} \quad \dots\dots\dots 3$$

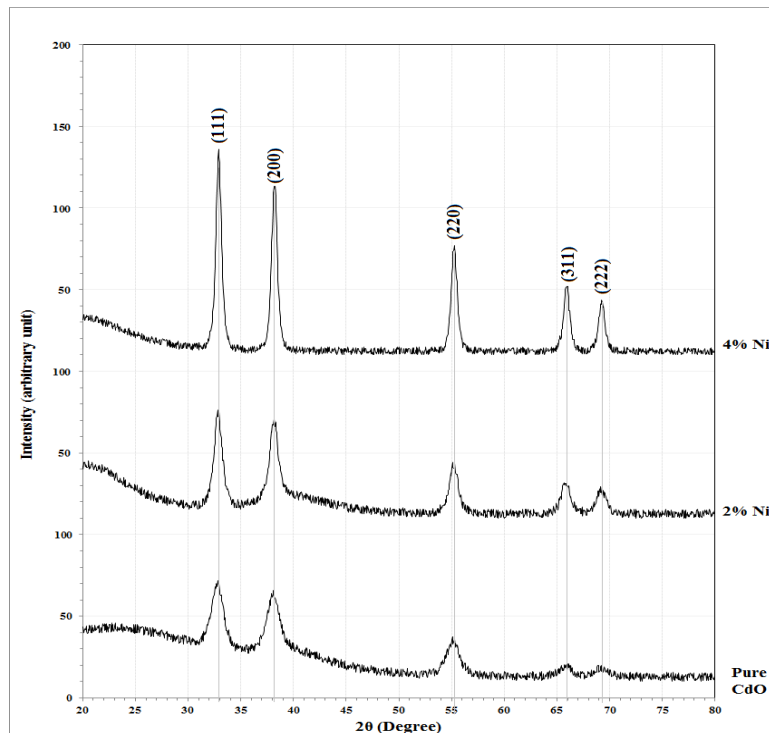


Fig. 1 X-ray diffraction patterns for pure and Ni doped CdO films with 2 and 4%.

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Fig. (2) shows two dimensional view for (111) and (200) peaks for pure and Ni doped CdO films with 2 and 4 wt% .It can be observed a slightly shift of peaks location toward higher value i.e decreasing in d_{hkl} spacing with increasing dopant ratio.

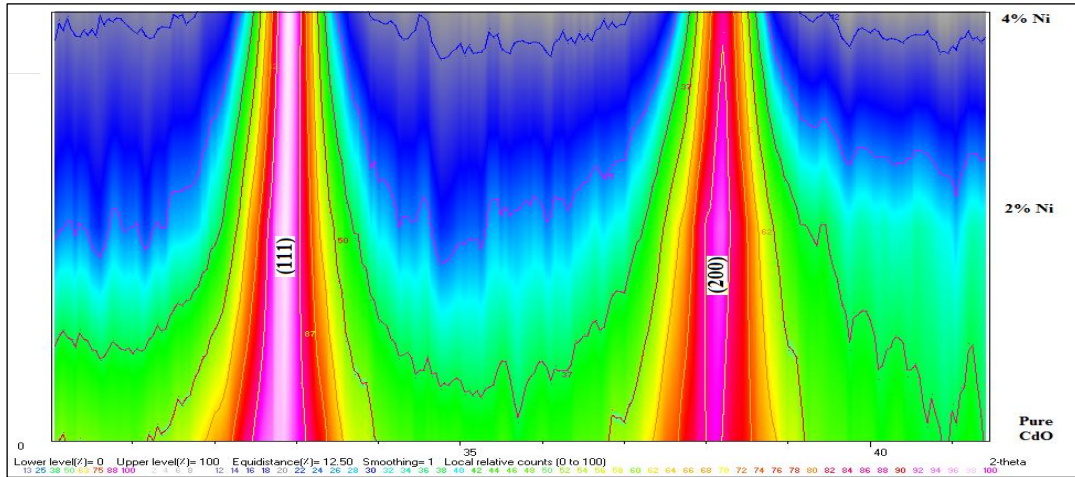


Fig. 2 2D view for (111) and (200) peaks for pure and Ni doped CdO films with 2 and 4%.

Gaussian fitting for all peaks were done to find the FWHM and then corrected by removing $K_{\alpha 2}$ and instrument broadening.

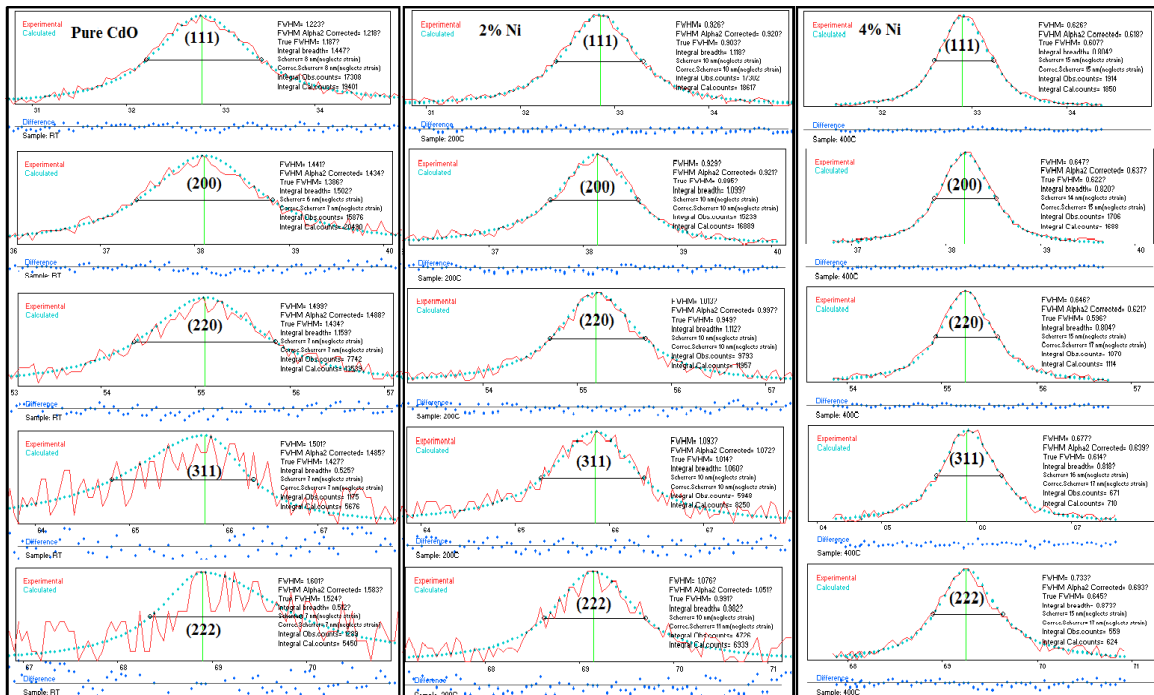


Fig.3 calculation of FWHM for all peaks for pure and Ni doped CdO films with 2 and 4%.

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Table (1) shows the experimental peaks, observe at XRD patterns, and the standard peaks from International center for diffraction data (JCPDS), corrected and uncorrected FWHM and grain size for pure and doped cadmium oxides films. It is clear that the doping leads to increase the grain size.

Table 1 Structural parameters for pure and Ni doped CdO films with 2 and 4%.

| Ni% | 2θ (degree) | d _{hkl} Exp.(Å) | d _{hkl} Std.(Å) | hkl | Observed FWHM (degree) | After K _{α2} and Instrumental Broadening Corrections (degree) | Uncorrected G.S (nm) | corrected G.S (nm) |
|-----|-------------|--------------------------|--------------------------|-------|------------------------|--|----------------------|--------------------|
| 0 | 32.7857 | 2.7294 | 2.7108 | (111) | 1.2234 | 1.1870 | 7.5 | 7.8 |
| | 38.0757 | 2.3615 | 2.3477 | (200) | 1.4408 | 1.3864 | 6.5 | 6.7 |
| | 55.1257 | 1.6647 | 1.6600 | (220) | 1.4994 | 1.4345 | 6.6 | 6.9 |
| | 65.7857 | 1.4184 | 1.4157 | (311) | 1.5013 | 1.4270 | 7.0 | 7.4 |
| | 69.1257 | 1.3578 | 1.3554 | (222) | 1.6006 | 1.5238 | 6.7 | 7.0 |
| 2 | 32.8547 | 2.7238 | 2.7108 | (111) | 0.9258 | 0.9029 | 9.9 | 10.2 |
| | 38.1447 | 2.3574 | 2.3477 | (200) | 0.9295 | 0.8952 | 10.0 | 10.4 |
| | 55.1947 | 1.6628 | 1.6600 | (220) | 1.0126 | 0.9489 | 9.8 | 10.5 |
| | 65.8547 | 1.4171 | 1.4157 | (311) | 1.0934 | 1.0138 | 9.6 | 10.4 |
| | 69.1947 | 1.3566 | 1.3554 | (222) | 1.0759 | 0.9914 | 10.0 | 10.8 |
| 4 | 32.9088 | 2.7195 | 2.7108 | (111) | 0.6262 | 0.6073 | 14.7 | 15.2 |
| | 38.1988 | 2.3542 | 2.3477 | (200) | 0.6473 | 0.6223 | 14.4 | 15.0 |
| | 55.2488 | 1.6613 | 1.6600 | (220) | 0.6457 | 0.5962 | 15.4 | 16.7 |
| | 65.9088 | 1.4161 | 1.4157 | (311) | 0.6771 | 0.6138 | 15.5 | 17.1 |
| | 69.2488 | 1.3557 | 1.3554 | (222) | 0.7333 | 0.6449 | 14.6 | 16.6 |

In order to obtain the true value of the lattice constant, we use Nelson-Riley function (*NRF*) defined by the following relation [11].

$$NRF = \frac{1}{2} \left[\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right] \dots \dots \dots (3)$$

where θ is the Bragg angle. The plot of a vs. *NRF* for the CdO film were plotted and extrapolation to *NRF*=0 yields the true parameter, a_0 .

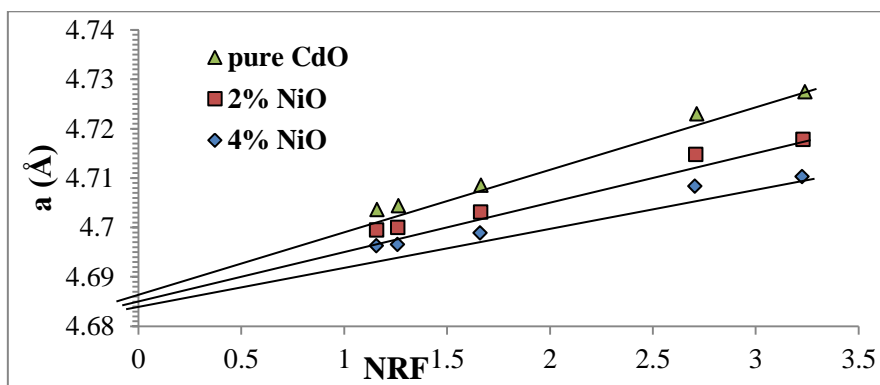


Fig.4 lattice constant for pure and Ni doped CdO films with 2 and 4%.NRF.

Table (2) illustrates experiment lattice parameter (a) deduced from XRD patterns using Nelson-Riley function. We can see that (a) decreased with increase the Ni content because the radius of Ni atom less than for Cd atom.

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Table 2 Experiment lattice parameter using Nelson-Riley function parameters for pure and Ni doped CdO films.

| Ni % | a (Å) |
|------|--------|
| 0 | 4.6893 |
| 2 | 4.6883 |
| 4 | 4.6875 |

Optical study of CdO films is carried out in the wavelength range 300–1100 nm for the film deposited on glass substrate. Figure (5) shows the transmission spectra of three samples at both values of Ni .

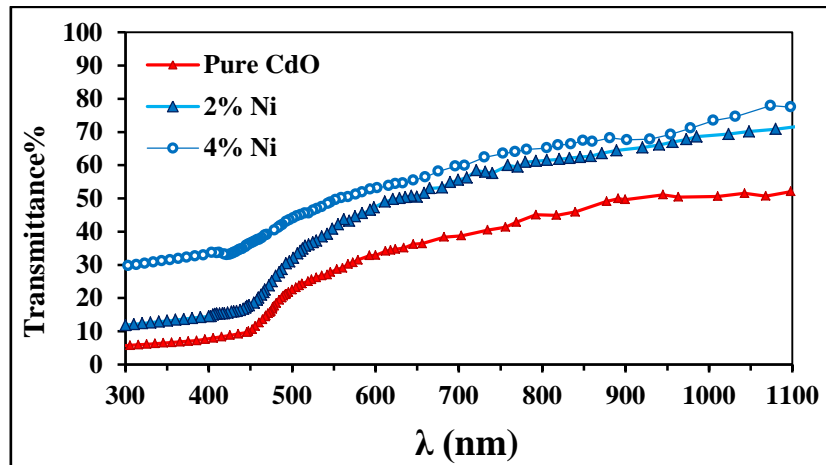


Fig.5 the transmission vs wavelength for pure and Ni doped CdO films with 2 and 4%.

The absorption coefficient (α) of cadmium oxides thin films were calculated from the optical transmittance spectrum measurements using the formula [12]:

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T} \right) \dots\dots\dots 3$$

where t is the thickness of thin films, and T is the transmittance intensity. The energy gap was calculated at both values of Ni .This is shown in Fig.(6).

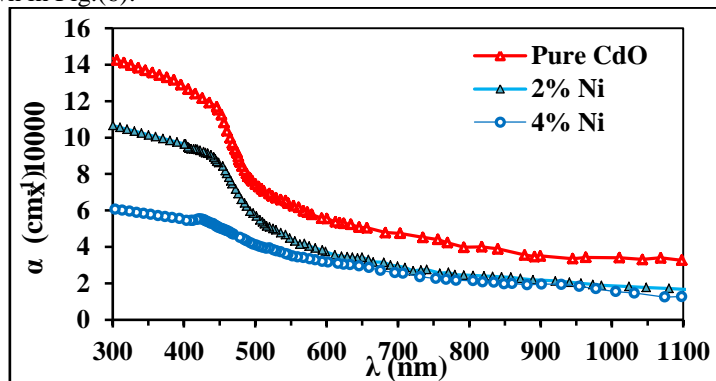


Fig.6 the absorption coefficient (α) with the wavelength for pure and Ni doped CdO films.

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The optical energy gap values (E_g) for cadmium oxide films have been determined by using Tauc equation. This is used to find the type of the optical transition by plotting the relations $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{1/3}$, $(\alpha h\nu)^{2/3}$, and $(\alpha h\nu)^2$ versus photon energy ($h\nu$). This equation also selects the optimum linear part. It is found that the relation for $r=1/2$ yields linear dependence, which describes the allowed direct transition. E_g is then determined by the extrapolation of the portion at $(\alpha = 0)$ as shown in figure (7).

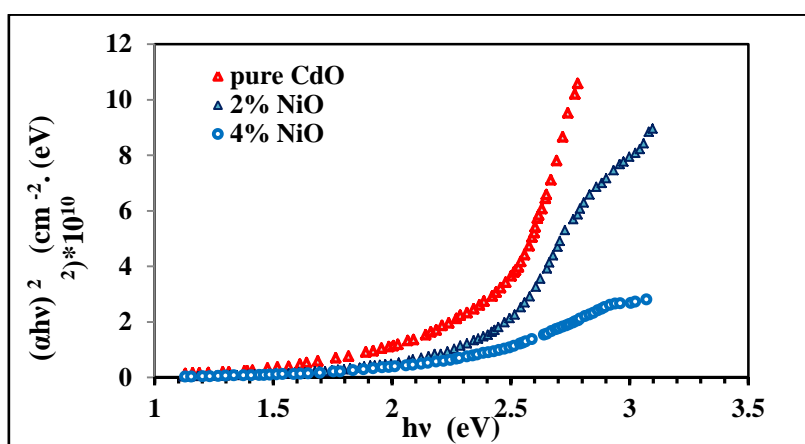


Fig. 7 The variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for pure and Ni doped CdO films with 2 and 4%.

Table (3) shows the influence of doping CdO film with Ni on the direct optical band gap. The pure CdO film deposited at 250 °C shows a band gap of 2.43 eV, while doping leads to decrease the energy gap to 2.24 eV for 4% Ni dopant ratio. The different in the calculated and reported energy gap values may be attributed to physical properties of the films, which are subsequently affected by the deposition conditions.

Table 3 Optical band gap values for cadmium oxide thin films with different Ni doping

| Ni % | E_g (eV) |
|------|------------|
| 0 | 2.43 |
| 2 | 2.35 |
| 4 | 2.24 |

IV. CONCLUSION

Structural and optical properties of pure and Ni doped CdO thin films deposited by spray pyrolysis deposition technique have been studied as a function of different Ni dopant concentrations. The outcome of this investigation can be summarized as follows:

- A polycrystalline structure are shown for pure and doped CdO films with Ni and have good identical with standard card for cubic CdO crystal.
- The films crystalline increases with increasing doping ratio.
- Crystallite size increases with increasing doping ratio.
- Lattice constant decreases with increasing doping ratio as a result of substitution of Ni instead of Cd ion.
- The transmittance increases with increasing Ni doping ratio.
- The energy gap decreases from 2.43 eV to 2.24 eV with the increase of Ni doping ratio from 0 to 4 %.

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