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Annealing Effect on Structural and Optical Properties of $Cd_{0.91}\ Ni_{0.09}$o Thin Films Prepared by Chemical Spray Pyrolysis

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Abstract

In this study, CdO:Ni thin films with 300 nm thickness and 9% nickel concentration were prepared by spray pyrolysis on glass substrates and annealed at different temperatures (350, 400 and 450) °C. The prepared films were characterized using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), and UV visible spectroscopy measurements in the wavelength (400-900) nm. XRD analysis exhibited a cubic crystalline structure. The crystalline size increased with the increase of temperature (23, 61,104,88) nm, also. The prepared annealed thin films showed high optical transmittance in the visible region The optical band gap energy (Eg) be found (2.51, 2.40, 2.27, and 2.22,) eV in before and after annealing temperature (350°C, 400°C and 450°C) respectively.

Keywords: Annealing, thin films, spray pyrolysis, X-ray diffraction.

دراسة تأثير التلدين على بعض الخصائص الفيزيائية لأغشية $(Cd_{1-x}\ Ni_xO)$ المحضرة بطريقة التحلل الحراري الكيميائي بالرش

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الخلاصة

تم تحضير اغشية $(Cd_{1-x}\ Ni_xO)$ بطريقة التحلل الحراري الكيميائي بالرش وكان الغشاء المحضر مطعم بالنيكل بنسبة (9%) وبسمك (300 nm)وتم تلدينه بدرجات حرار مختلفة (350°C, 400°C, and 450°C). درست الخصائص التركيبية للأغشية المحضرة بواسطة جهاز حيود الاشعة السينية (XRD) والمجهر الالكتروني الباعث (FE-SEM) ووجدت ان الاغشية المحضرة ذات تركيب متعدد التبلور وبنية تركيبية مكعبة وان الحجم البلوري يزداد بزيادة درجة حرارة التلدين (23–104) nmوتمت دراسة الخصائص البصرية بواسطة جهاز (UV-VIS) حيث بينت النتائج انه بزيادة درجة حرارة التلدين تزداد نفاذية الاغشية وتقل نسبة فجوة الطاقة eV (2.51, 2.40, 2.27, and 2.22).

الكلمات المفتاحية: التلدين ، الاغشية الرقيقة، التحلل الحراري الكيميائي بالرش، حيود الاشعة السينية.

Introduction

The importance of Transparent Conductive Oxide (TCO) thin films in optoelectronic devices cannot be understated. Initially used mainly as electrodes in early electronics, TCOs have seen significant growth in various applications in recent years, such as displays, light-emitting diodes, and thin film solar cells [1,2]. At room temperature, TCOs exhibit unique properties. Among the most widely used TCOs are ternary oxides like In-doped SnO2, In-doped CdO, and F-doped SnO2 [3]. Doped CdO, a transparent conductive oxide material, has been extensively studied and is capable of being produced as thin films. These films find applications in diverse areas, including solar cells [4], phototransistors [5], photodiodes [6], transparent electrodes [7], and gas sensors [8]. Various processes can be employed to produce CdO films, such as sputtering [11], chemical vapor deposition (CVD) [12], thermal pyrolysis [13], thermal evaporation [14], and sol-gel [15]. Meanwhile, Nickel oxide (NiO), a selective oxide, has garnered significant attention. It is a p-type semiconductor with a cubic crystal structure and an energy band gap of Eg = 3.6-4 eV, making it suitable for applications like solar heat absorption [16,17], oxygen evolution catalysis [18], image electrolysis [19], electrochromic [20], and chemical sensors [21]. NiO can be deposited using various techniques, such as chemical bath deposition [23], pyrolysis spraying [24], sol-gel processes [25], atomic layer deposition [26], pulsed laser deposition [27], organic chemical vapor deposition [28], beam molecular radial [29], DC [30] and RF magnetrons, and electrodes [31], among others methods, chemical spray pyrolysis stands out as a cost-effective production process that utilizes simpler equipment. The resulting thin films exhibit favorable properties and find numerous applications in research, technical, and industrial fields [32]. This study focuses on investigating the impact of annealing on the structural and optical properties of pyrolyzed CdO thin films. The results hold promise for further enhancing the applications and performance of these thin films in various optoelectronic devices.

Experimental details

Ni-doped CdO films were fabricated on glass substrates using a chemical spray pyrolysis method at a deposition temperature of 400 °C. The Ni content in the CdO film was 9% by weight, achieved by introducing cadmium nitrate ($Cd(NO_3)_2.4H_2O$) and nickel nitrate ($Ni(NO_3)_2.6H_2O$) obtained from Glentham life sciences. These chemicals were mixed at a concentration of 0.2 mol% in 100 ml of distilled water. To ensure a clean substrate surface essential for nucleation centers' formation during deposition, the glass substrate slides (2.5-2.5 cm) were first cleaned in an ultrasonic bath with acetone solution for 5 minutes. They were then rinsed with distilled water and dried using a special cloth to remove any impurities. The final solution for deposition was prepared by blending the two starting solutions in appropriate volume ratios to achieve the desired Ni concentration of 9 wt%. This solution was then sprayed onto heated glass substrate to (400°C) with specific deposition conditions, including a nozzle to substrate distance of 30 cm, a sputtering time of 6 seconds, a sputtering interval of 2 minutes, and a carrier gas pressure of 1.5 bar. Subsequently, the produced thin films were subjected to annealing at different temperatures, specifically 350 °C, 400 °C, and 450 °C, for a duration of 1 hour using an electric furnace manufactured by LabTEch, Korea. This annealing process plays a crucial role in modifying the structural properties of the Ni-doped CdO films, making them suitable for various optoelectronic applications.

Results and Discussion

Structural properties

Figure 1 illustrates the X-ray diffraction (XRD) patterns of CdO thin films in both the as-deposited state and after annealing at temperatures of 350°C, 400°C, and 450°C for a duration of 1 hour. The XRD analysis employed Cu Kα radiation (λ=1.5406Å nm) and covered a Bragg angle range of 30° to 80° (2θ). The XRD pattern confirms the polycrystalline nature of the CdO:9%Ni phase, exhibiting a cubic crystal structure. Notably, the XRD pattern reveals prominent peaks at 2θ=33° and 38°, corresponding to crystal planes (111) and (200), respectively. Additionally, there are weaker peaks observed at 2θ=55°, 65.9°, and 69°, corresponding to crystal planes (220), (311), and (222), respectively. These findings are consistent with the data reported in the (ICDD) card no. (75-0592) [33].

Upon closer examination of Figure 1, it is evident that the intensity of the diffraction peaks increases with the rise in annealing temperature, while the full width at half-maximum (FWHM) decreases, indicating an improvement in the crystalline quality. The most intense peak at 33° suggests a preferred orientation of the CdO thin films along the (111) crystallographic plane.

The lattice constant (a°) was calculated using the following Formula:

$$d_{hkl} = a_{\circ}/\sqrt{h^2 + k^2 + l^2} \qquad (1)$$

Where (d_{hkl}) is the interplanar distance of the crystals, (a°) is the lattice constant and (hkl) is the Miller index.

These XRD results offer valuable insights into the structural properties of the Ni-doped CdO thin films, shedding light on their crystallographic orientation and demonstrating the impact of annealing temperature on their crystalline characteristics.

The average grain size (D) was estimated using the Scherrer formula [34]:

$$D_{av} = \frac{0.9\lambda}{\beta \cos\theta_B} \qquad (2)$$

Where β is the full width at half maximum of the (111) peak measured in radians, λ is the used wavelength and θ is the Bragg angle.

and the dislocation density (δ) was calculated using the following relationship [34]:

$$\delta = 1/D^2 \qquad (3)$$

The results indicate that the crystallite size, as determined from the peak (111), exhibited an increase (from 61 to 104 nm) in samples annealed at temperatures of 350°C, 400°C, and 450°C. This observed increase in crystallite size can be attributed to the enhancement in crystal quality. However, a decrease in crystallite size was observed when the annealing temperature was further raised to 400°C. Additionally, the number of crystallites (N○) was calculated using the following relationship:

$$N_o = t/D^3$$

Where N_o is the number of crystallites and t is the thickness.

It's found that (N○) was decreased as the annealing temperature increased for samples annealed at 350°C and 450°C, and this trend continued up to 400°C. These changes in crystallite size and number of crystallites are likely the result of the periodic arrangement of atoms in the crystal lattice and the overall improvement in crystal quality.

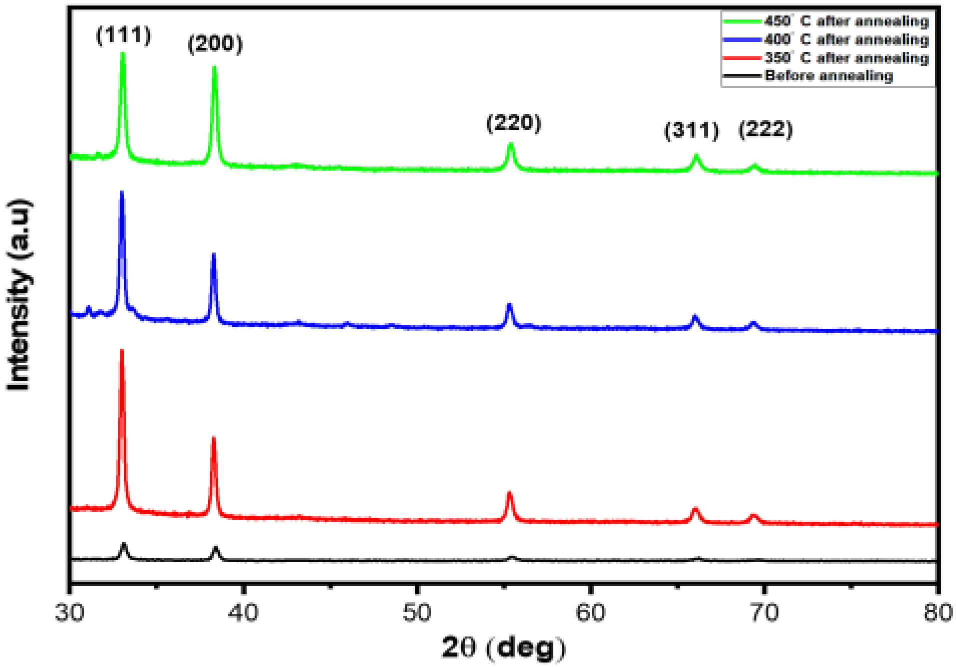

Figure 1: Structural Parameters of CdO: Ni for Different Values for (350°C, 400°C and 450°C).

Table 1: The following table presents the structural parameters of CdO: Ni for various values of (350°C, 400°C and 450°C).of x.

Sample	(hkl)	2θ (°)	FWHM(°)	Lattice Constant 'a' (Å)	Interplanar Spacing 'd' (Å)	volume	Average D (nm)	δ (nm^{-2})	N○ (nm^{-2})
Before annealing	(111)	33.1302	0.3655	4.679	2.701	102.48	23.69	1.78	0.17
350 ℃	(111)	33.0055	0.1407	4.696	2.711	103.61	61.53	0.26	0.0097
400 ℃	(111)	33.0419	0.0792	4.691	2.708	103.28	104.67	0.17	0.0017
450 ℃	(111)	33.0223	0.0974	4.694	2.710	103.46	88.89	0.12	0.0032

Morphological characterizations

Field Emission Scanning Electron Microscopy (FE-SEM)for CdO: Ni thin films

FE-SEM, a convenient technique for studying thin film surface morphology, was employed to analyze CdO: Ni thin films before and after annealing, as shown in Fig. 2. The FE-SEM micrographs of the CdO: Ni thin film before annealing revealed a homogeneous dispersion of cubical and oblique crystal structures [35]. Additionally, the FE-SEM images exhibited compact, dense CdO films adhered to the entire substrate without any cracks.The observed grain size (D) from FE-SEM was found to be larger than the size determined by Scherrer's formula, as indicated in Table 2. This suggests that large grains comprise multiple smaller crystallites, each with a size determined by Scherrer's formula. Notably, the surface properties of the CdO films appeared to change with annealing temperature (TA). After annealing, the FE-SEM images demonstrated an increase in crystallinity, although the surface did not become smooth. This indicated that sputtered particles adsorb on the sample surface, forming clusters during the initial stages of nucleation. These clusters are composed of particles with higher energy than single atoms. As the annealing temperature increases, the growing nuclei come into contact and form island-like patterns with a spherical appearance [36]. Even at a relatively low annealing temperature of 450 °C, a spherical morphology of the CdO thin film was observed. This spherical morphology may offer potential advantages for solar cell applications.

Table 2: FESEM grain size

Samples	Grain size (nm)
Cd:9%Nio	38nm
Annealed 350℃	45nm
Annealed 400℃	48nm
Annealed 450℃	49nm

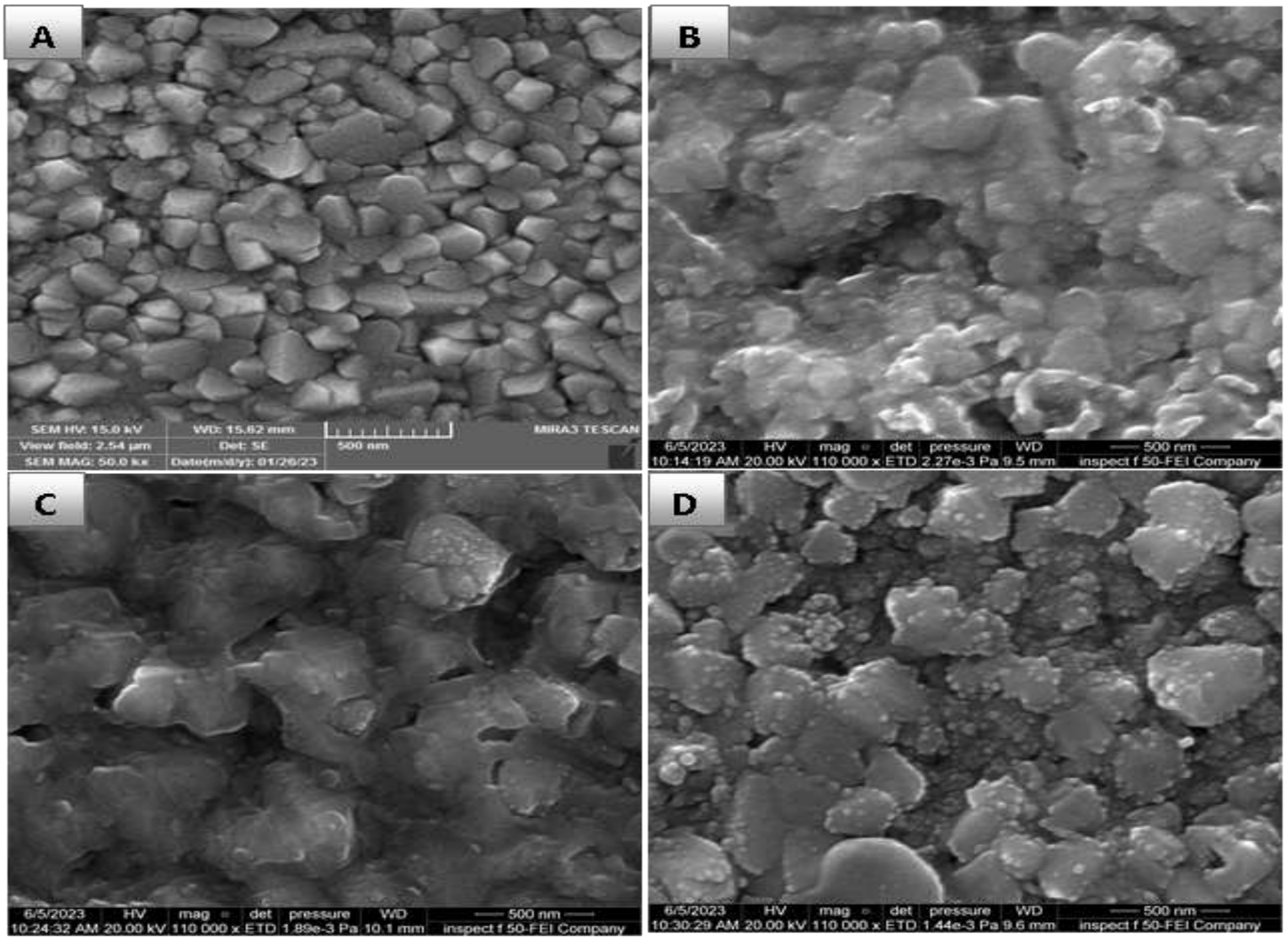

Figure 2: Fe-SEM images of CdO:Ni thin films A. before annealing B.after annealing 350°C C. after annealing 400°C D.after annealing 450°C

Optical properties

In this study, we present the optical measurement results of Ni-doped CdO thin films annealed at different temperatures (350°C, 400°C, and 450°C), focusing on the relationship between transmittance, absorbance, and wavelength, as well as certain optical constants. Fig. 3a

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illustrates that the optical absorbance of CdO thin films decreases with increasing wavelength and rises with higher post-annealing temperatures. This phenomenon can be attributed to the band-to-band transition occurring between the conduction band and ionized donor [37]. Notably, the films exhibit higher absorbance in the lower-visible region compared to the higher-visible region. The transmission spectra of CdO thin films (Fig. 3b) reveal that transmittance increases with higher wavelengths. However, it decreases with annealing within the visible range and then displays interference fringe behavior due to the removal of defects, as observed in all films in the higher visible range. Interestingly, films with lower density of grain boundaries exhibit higher transmittance, leading to improved film stoichiometry at higher annealing temperatures, accompanied by a reduction in the number of defects [38]. The ability of the material to absorb light is measured by its direct absorption coefficient (α), which can be determined using the equation: $\alpha = \ln(1/T) / t$ (where T is the transmittance and t is the film thickness). Figure 4 depicts the variation of the absorption coefficient with wavelength, indicating a decrease in the absorption of Ni-doped CdO thin films with increasing annealing temperature. The thin film displays an absorption edge around 600 nm, and this edge shifts slightly towards higher wavelengths as the annealing temperature rises [39,40].

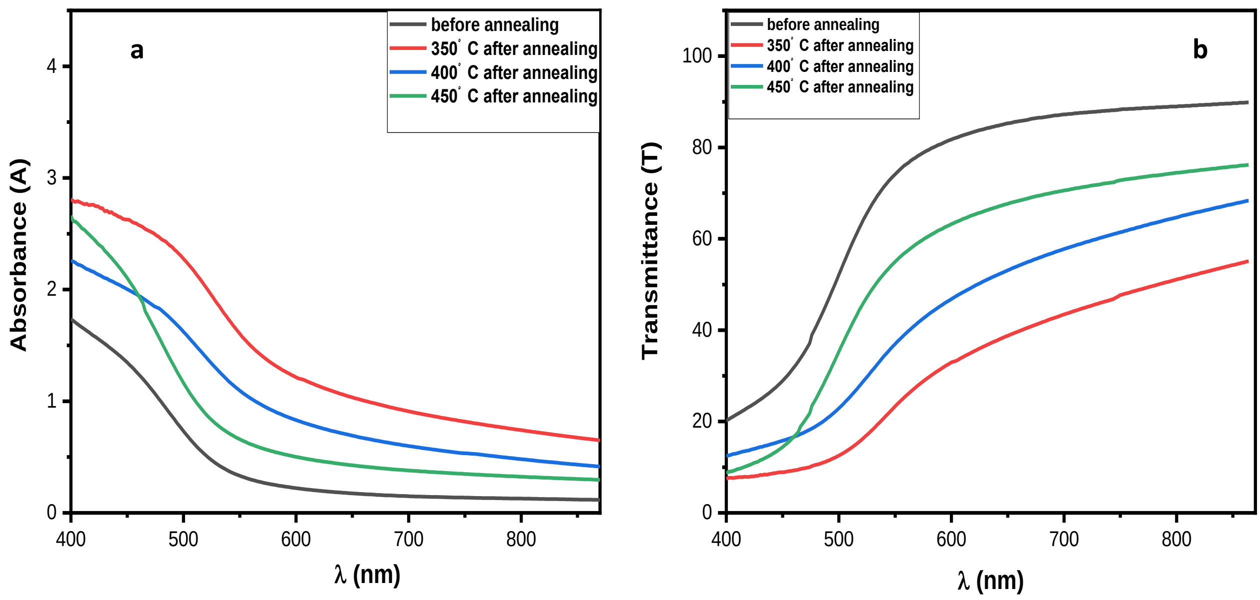


Figure 3: (a) Optical absorbance and (b) transmittance of CdO thin films

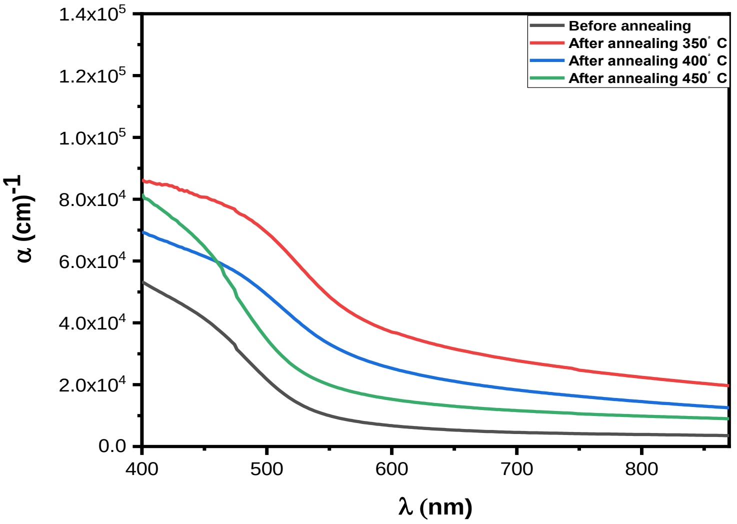
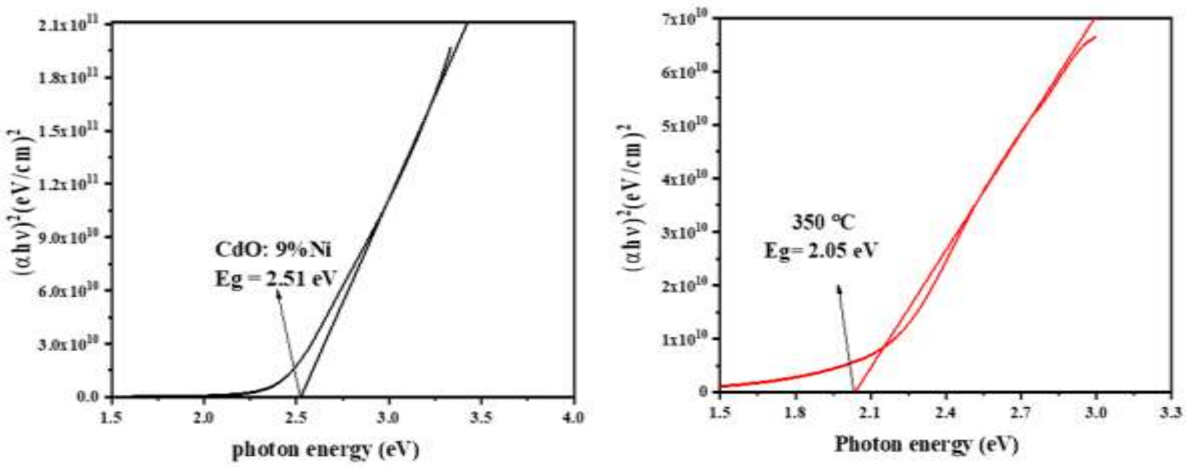


Figure 4: Absorption co-efficient spectra of annealed CdO:Ni thin films

Previously, another author had prepared CdO thin films that exhibited direct transitions [41,42]. The direct optical bandgap of the annealed Ni-doped CdO thin film sample was determined by extrapolating the linear portion of the (αhν)^2 versus hν plot to the hν axis, as illustrated in Figure 5.

Table 3 presents the allowable direct transition band gap values, showing that the CdO thin film's direct transition band gap decreases (2.5eV,2.05eV, 2.2 eV, and 2.4eV) respectively with increasing annealing temperature. This decrease in the direct transition band gap is attributed to the improvement of the crystal structure and an increase in grain size [43,44]. This trend aligns with the findings reported by Aksoy et al. [45].



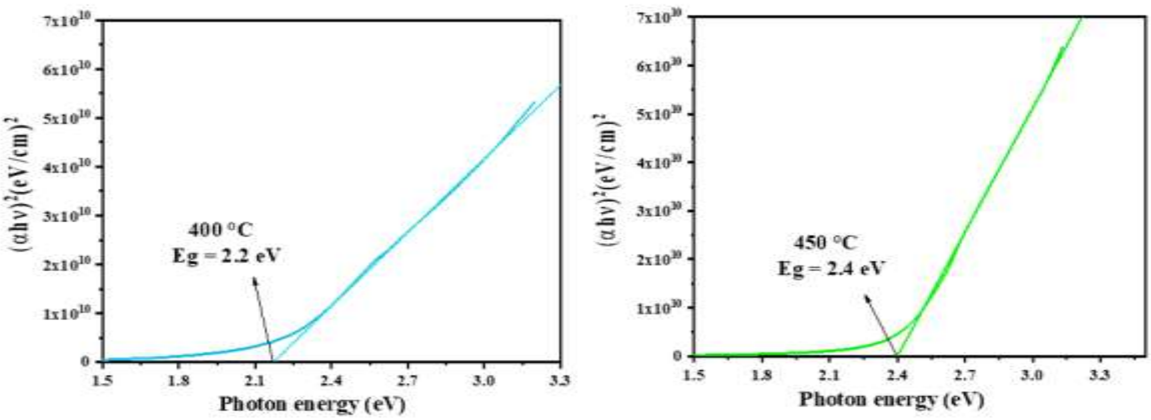


Figure 6: Band gap determination of annealed CdO:Ni thin films.

Table 3: Band gap of annealed CdO:Ni thin films

Samples	band gap E_g
Cd:9%Nio	2.51ev
Annealed 350℃	2.05eV
Annealed 400℃	2.2eV
Annealed 450℃	2.4eV

Conclusions

In this investigation, CdO thin films were synthesized using cadmium nitrate tetrahydrate and nickel (II) nitrate hexahydrate as sources for cadmium and nickel respectively by spray pyrolysis method. X-ray diffraction analysis revealed that all CdO thin film samples exhibited a polycrystalline nature, characterized by a cubic structure. Furthermore, the crystallite size of the films showed enhancement with increasing annealing temperature (from 61 to 104 nm). Inhansing of the grain size for the annealed films was further confirmed via SEM analyses. The surface morphology based on the SEM results exhibited that, the average grain size of the films around (39-48) nm. Remarkably, all the annealed thin films demonstrated excellent optical transmittance in the visible region (400-900 nm), making them highly transparent. Based on these findings, it can be concluded that Ni-doped CdO thin films annealed at 350°C exhibit favorable attributes, including good crystallinity, high transparency, these properties make them promising candidates for various technical applications, particularly in the field of solar cells.

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