



Ni Doping Effects On The Structural And Optical Properties Of Cds Thin Films Fabricated By Spray Pyrolysis

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In this study, nickel-doped cadmium sulfide (CdS) thin films were produced using the spray pyrolysis technique. Nickel doping concentrations were adjusted to include undoped samples as well as 1%, 2%, 3%, 4%, and 5% ratios. The structural, optical, and morphological characteristics of the films were examined using techniques such as X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectroscopy, and scanning electron microscopy (SEM). These methods provided comprehensive insights into the films' properties. The XRD results indicated the crystalline nature and phase purity of the films, demonstrating that incorporation of nickel affected both the crystallite size and preferred orientation. UV-Vis spectroscopy was used to study the optical properties, with the bandgap energy shifting in response to varying nickel concentrations. SEM images provided information on surface morphology and grain size changes, offering insights into how doping affects film quality. These findings demonstrate the potential of nickel doping in modifying the characteristics of CdS thin films for optoelectronic operations.

Keywords: Nickel doping, Cadmium sulfide(CdS), Spray pyrolysis, Thin Films

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1. Introduction

Cadmium sulfide (CdS) films are widely regarded as efficient optical layers due to their broad bandgap energy of around 2.420 eV at room temperature. This characteristic makes them highly suitable for numerous applications, like in photovoltaics[1][2]. Recently, increasing the electrical performance of CdS has become particularly important for enhancing the performance of optoelectronic instruments. A common method to achieve this improvement is through doping, where metal atoms are incorporated into CdS thin films to create materials with lower resistivity.[3].

There has been considerable research focused on enhancing the features of CdS films through some impurity additions with various elements, like (In³⁺)[4], (Al³⁺)[5], (Ga³⁺)[6], and (La³⁺)[7]. These studies have shown that doping can significantly alter the electronic and optical characteristics of films, often leading to improved performance in optoelectronic applications. Compared to CdS films that have been doped with transition metal elements like Mn²⁺,

Fe²⁺, and Ni²⁺, the available data is still quite limited. Further research is needed to fill this gap and provide a deeper understanding of the material's properties. Such insights are crucial for understanding how different doping elements can influence the efficiency of CdS-based devices.

Nickel, a crucial transition metal with an ionic radius of 0.620 Å, is smaller than that of Cd²⁺ (0.970 Å). This size difference allows Ni²⁺ ions to seamlessly integrate into the CdS crystal lattice, replacing Cd²⁺ ions and improving the physical properties of the material. The incorporation of smaller Ni²⁺ ions can lead to less strain within the lattice, resulting in better crystallinity. Ni as a promising dopant to boost the performance of CdS films in photovoltaic applications, potentially leading to higher energy conversion rates and better overall device performance[4].

A variety of models were effectively utilized for the fabrication of CdS and metal-doped CdS films, including. This approach is especially preferred due to its straightforwardness and ability to fabricate homogenous films over large areas. In particular, there has been

considerable focus on exploring the effect of Ni doping on the structural and magnetic features of CdS films. Previous research has indicated that Ni doping can significantly alter the band structure, leading to enhanced optical properties. Consequently, this study intends to examine some physical characteristics of Ni-doped CdS thin films, aiming to provide deeper insights into how Ni influences the overall performance of the material in various applications.

2. Experimental Studies

2.1. Materials and Manufacturing

To enhance the properties of the CdS films, nickel (Ni) was incorporated as a dopant during the fabrication process. Ni-doped CdS thin films have been fabricated onto glass employing the spray pyrolysis method. The precursor solutions were created by dissolving cadmium acetate ($\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$), sulfur (S), and nickel acetate ($\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$) in deionized water, with quantities adjusted based on the calculated ratios for each sample. To modify the film compositions, different amounts of Ni were incorporated into the solution while maintaining a constant stoichiometric ratio of sulfur. The molar concentrations of nickel has been changed to explore their effects regarding structural and optical features of the films.

Before deposition, all substrates underwent an extensive cleaning procedure to remove any contaminants and ensure proper adhesion of the films. This cleaning process included rinsing with acetone, ethanol, and deionized water, followed by ultrasonic cleaning. Afterward, the substrates were air-dried in preparation for film deposition.

2.2. Spray Pyrolysis Deposition

The spray pyrolysis system used in this study is a simple yet highly effective configuration that includes essential components such as a nozzle, a container for the precursor solution, and a heated substrate holder. Compressed air was employed to facilitate the atomization of the precursor solutions. The glass substrates were heated to around 350°C , onto which the precursor solution was sprayed uniformly. Ensuring homogeneous and consistent film thickness is vital for optimizing the physical features of thin films. Therefore, careful control of the solution flow rate and spraying duration was implemented to achieve uniform thickness across the deposited films. Throughout the deposition process, maintaining stable environmental conditions and experimental parameters was a priority. The nozzle-substrate distance was meticulously set to 20 cm to optimize atomization and deposition efficiency.

3. Result and Discussions

3.1. X-Ray Diffraction Studies

Figure 1 illustrates the X-ray diffraction (XRD) patterns of Ni-doped and undoped CdS thin films fabricated at various Ni concentrations. The distinct peaks observed in the diffraction patterns correspond to the crystalline phases

present in the films. XRD analysis was performed to assess the crystallographic structure and phase purity of the CdS and Ni-doped CdS films. This analysis is crucial for determining how doping affects the crystallinity and structural integrity of the material. Measurements have been performed employing a diffractometer operating at a wavelength of 1.5406 \AA . The use of this specific wavelength allows for accurate identification of the crystal phases. The scanning range was established from 20° to 80° (2θ) to capture the diffraction patterns of the samples, ensuring that a comprehensive analysis of the structural characteristics was obtained.

The diffraction peaks in the XRD patterns were analyzed to ascertain the crystalline structure, crystallite size, and preferred orientation of the films. The positions of the diffraction peaks were compared against standard reference patterns from the JCPDS database to identify the phases present in the films.

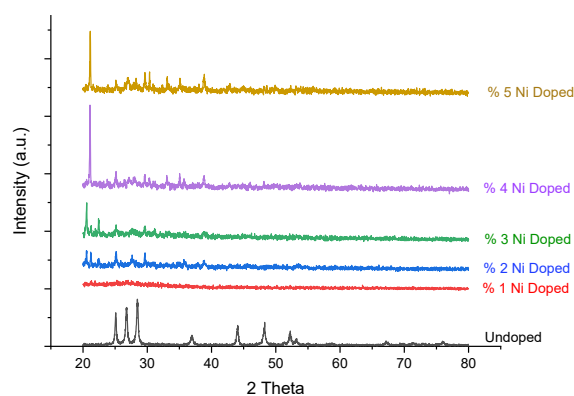


Figure 1: X-ray diffraction (XRD) patterns of undoped and Ni doped CdS thin films produced via the spray pyrolysis method.

The XRD pattern reveals a significant finding: the disappearance of CdS peaks accompanied by the emergence of new peaks in the doped films. Furthermore, while the undoped CdS film displays multiple peaks, the doped films feature a single dominant peak. This observation indicates a structural transition or phase change in the material due to the doping process.

Several key insights can be drawn from the XRD patterns concerning the effect of Ni doping on the structural properties of CdS thin films. As the concentration of Ni doping increases, notable changes occur in the XRD peaks, including the vanishing of several CdS peaks, the appearance of new peaks, and the predominance of one significant peak in the doped films. Additionally, there is a noticeable trend of increasing peak intensity with higher Ni doping concentrations. This trend can be explained as follows:

The absence of characteristic CdS peaks and the appearance of new peaks in the doped films indicate a notable structural transformation. The incorporation of Ni atoms seems to have modified the crystal structure of CdS, potentially resulting in a phase transition or the creation of Ni-rich secondary

phases. This alteration could suppress the original CdS diffraction peaks while giving rise to new peaks linked to these secondary phases. The prominent single peak observed in the doped films may suggest a dominant crystallographic plane or preferred orientation within the modified structure.[5].

The observed increase in peak intensity with higher Ni doping concentrations suggests an improvement in the crystalline quality of the doped films. This enhancement in crystallinity may stem from several factors: the incorporation of Ni atoms into the crystal lattice, which diminishes defects and imperfections, resulting in a more ordered structure and stronger diffraction signals; the development of a Ni-rich phase at elevated concentrations, which contributes to greater crystallinity compared to undoped CdS; and the stabilization of the lattice by the dopant atoms, which reduces microstrain and enhances the material's crystalline characteristics. Together, these effects lead to narrower and more intense XRD peaks, indicating a reduction in structural disorder[5].

The reduction in the number of peaks from multiple peaks in the undoped film to a single peak in the doped films suggests a shift towards a more uniform or preferred crystallographic orientation. This could imply that, with increasing Ni content, the crystallites grow predominantly along one specific direction, which would account for the dominance of a single diffraction peak. The decrease in the number of peaks, transitioning from multiple peaks in the undoped film to a single peak in the doped films, indicates a movement towards a more uniform or preferred crystallographic orientation. This suggests that as the Ni content increases, the crystallites tend to grow primarily in one specific direction, explaining the predominance of a single diffraction peak.

3.2. Optical Studies

Optical studies are essential for gaining insights into the fundamental properties of materials, especially in the semiconductor domain. These investigations focus on how materials interact with light, revealing details about their electronic structures, band gaps, and defect states. By utilizing techniques such as UV-Vis spectroscopy, photoluminescence, and ellipsometry, researchers can analyze the absorption, emission, and refractive characteristics of various semiconductor materials. This knowledge is crucial for enhancing their performance across a wide array of applications, including photovoltaics, light-emitting diodes (LEDs), and photodetectors. Cadmium sulfide (CdS), in particular, is of great interest due to its advantageous optical properties, making it a promising candidate for cutting-edge optoelectronic devices. Through thorough optical investigations, the design and development of more efficient and innovative technologies can be significantly improved[6].

In this study, we concentrate on the optical properties of cadmium sulfide (CdS) thin films, specifically exploring how different doping levels and synthesis methods affect

their performance. By employing advanced characterization techniques such as UV-Vis spectroscopy and photoluminescence, we aim to assess the band gap energy, absorption characteristics, and emission behavior of the CdS films.

We investigate the impact of nickel (Ni) doping on the optical properties, studying how different doping concentrations influence the material's crystallinity and, consequently, its optical behavior. Our goal is to uncover the fundamental mechanisms behind these changes, with the aim of optimizing CdS for applications in photovoltaic devices and optoelectronics. Through our findings, we hope to offer valuable insights that contribute to the improvement of more efficient and high-performance semiconductor materials for advanced technological applications.

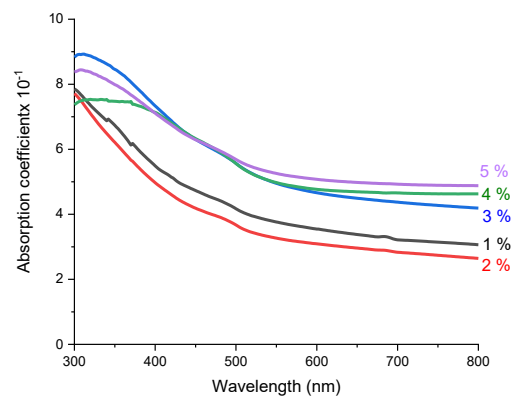


Figure 2: Absorption spectra of the Ni doped CdS thin films

UV-Vis spectroscopy was employed to investigate the optical properties of Ni-doped CdS thin films. The absorbance profiles for the films synthesized with different Ni concentrations are presented in Fig. 2. All films demonstrated considerable absorption in the 300-800 nm range, with a noticeable shift in the absorption edge as the Ni content increased. This shift suggests variations in the optical bandgap of the films in response to changes in the Ni doping ratio.

The optical bandgap (E_g) figures for the films were calculated based on the relationship between the absorption coefficient (α) and the photon energy ($h\nu$), which can be expressed as follows[7]:

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

In this context, where A is defined as a coefficient related to the effective masses, the bandgap values are calculated from the plots of $(\alpha h\nu)^2$ against $h\nu$ by extrapolating the linear portion of the line to the energy axis at $\alpha = 0$ (Figure 3).

The initial reduction in the band gap with increasing Ni content, followed by a subsequent increase, can be explained

by alterations in the material's structure and electronic properties.

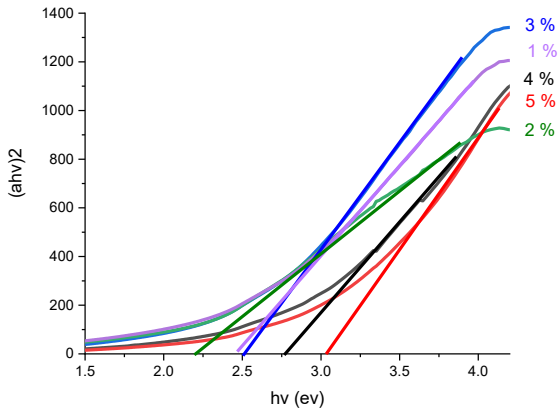


Figure 3: Plots of $(\alpha hv)^2$ vs. $h\nu$ of the Ni doped thin films.

At lower concentrations of Ni, alloying effects and crystal defects contribute to a decrease in the band gap by modifying the energy levels of the conduction and valence bands and introducing disorder into the crystal lattice.

3.3. Surface Morphology Analysis of PbZnS Thin Films

To gain a deeper understanding of the surface morphology and microstructural features of the undoped and Ni-doped thin films, scanning electron microscopy (SEM) was utilized. The SEM images offer valuable insights into grain distribution, surface roughness, and the impact of varying Ni concentrations on the film structure.

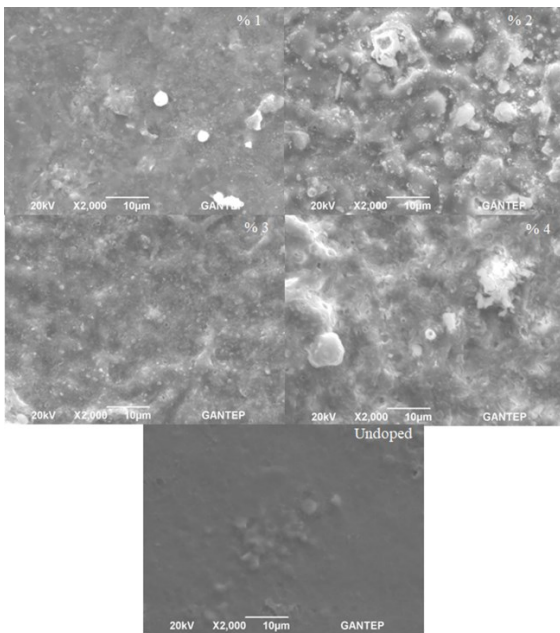


Figure 4: SEM images of Ni-doped CdS films.

The SEM images show slight surface irregularities and protrusions; however, no visible cracks or fractures are

detected. These surface characteristics suggest minor morphological differences, possibly resulting from localized stress or the growth conditions during the deposition process. The lack of cracks indicates that the film retains its structural integrity, which is a favorable sign for its mechanical stability. Additionally, these findings are consistent with the XRD results, which likely point to a uniform crystalline phase. The agreement between the SEM and XRD analyses suggests that, despite minor surface imperfections, the overall crystallinity and phase purity of the material are well-preserved, indicating good material quality.

4. Conclusion

In this research, Ni-doped CdS thin films were successfully produced using the spray pyrolysis technique, with Ni doping concentrations ranging from 0% to 5%. This method was chosen for its ability to create uniform and adherent films on various substrates. The impact of nickel incorporation on the structural, optical, and morphological properties of the films was thoroughly investigated through XRD, UV-Vis spectroscopy, and SEM techniques. These characterization methods provide valuable insights into how doping alters the material's behavior. The results obtained from XRD allowed for the determination of crystal structure and phase purity, while UV-Vis spectroscopy enabled the assessment of optical properties such as absorbance and bandgap energy. Additionally, SEM analysis offered a detailed view of the surface morphology, revealing the effects of Ni doping on film texture and grain size.

XRD analysis revealed notable alterations in the crystallographic structure due to Ni doping, including the loss of multiple peaks from the undoped CdS and the appearance of a single dominant peak in the doped films. This observation suggests a structural transformation and potential phase transitions triggered by the incorporation of Ni. The increase in peak intensity with higher Ni concentrations indicates enhanced crystallinity, while the shift in peak position and peak narrowing point to a reduction in microstrain and defects within the crystal lattice.

The results from UV-Vis spectroscopy exhibited a clear trend in the optical properties, with Ni doping causing shifts in the absorption edge and variations in the optical bandgap energy. The bandgap initially decreased with increasing Ni content but later increased at higher doping levels. This behavior can be attributed to the influence of Ni on the films' electronic structure, impacting both alloying effects and defect states.

SEM images indicated that the surface structure varied with Ni concentration, showing slight surface irregularities but no

visible cracks or fractures. The consistent grain distribution and absence of significant surface defects suggest that Ni doping enhances the mechanical stability of the films, supporting the findings from XRD and optical analyses.

Overall, this study underscores the potential of Ni doping in tuning the structural and optical properties of CdS thin films. The ability to adjust the bandgap and achieve improved crystallinity through Ni incorporation positions these films as promising candidates for optoelectronic applications, particularly in photovoltaic devices. Future research should further investigate the electrical characteristics of Ni-doped CdS films to fully assess their potential in energy conversion and other semiconductor technologies.

References

- [1] Plesco I, Dragoman M, Strobel J, et al (2018) Flexible pressure sensor based on graphene aerogel microstructures functionalized with CdS nanocrystalline thin film. *Superlattices Microstruct* 117:418–422. <https://doi.org/10.1016/J.SPML.2018.03.064>
- [2] Priya NS, Kamala SSP, Anbarasu V, et al (2018) Characterization of CdS thin films and nanoparticles by a simple Chemical Bath Technique. *Mater Lett* 220:161–164. <https://doi.org/10.1016/J.MATLET.2018.03.009>
- [3] El Radaf IM, Hameed TA, Yahia IS (2018) Synthesis and characterization of F-doped CdS thin films by spray pyrolysis for photovoltaic applications. *Mater Res Express* 5:066416. <https://doi.org/10.1088/2053-1591/AACA7B>
- [4] Sakr GB, Yahia IS, El-Komy GM, Salem AM (2011) Optical properties of thermally evaporated Bi₂Se₃ thin films treated with AgNO₃ solution. *Surf Coatings Technol* 205:3553–3558. <https://doi.org/10.1016/J.SURFCOAT.2010.12.013>
- [5] Yılmaz S, Tomakin M, Ünverdi A, et al (2020) Structural, morphological, optical analyses of Ni-doped CdS thin films and their photovoltaic performance in hybrid solar cells. *J Mater Sci Mater Electron* 31:12932–12942. <https://doi.org/10.1007/S10854-020-03846-1/TABLES/2>
- [6] Razeghi M (2009) *Fundamentals of solid state engineering*, 3rd edition
- [7] Ravishankar S, Balu AR, Anbarasi M, Nagarethinam VS (2015) Influence of precursor molar concentration on the structural, morphological, optical and electrical properties of PbS thin films deposited by spray pyrolysis technique using perfume atomizer. *Optik (Stuttg)* 126:2550–2555. <https://doi.org/10.1016/J.IJLEO.2015.06.039>