Unal, F. (2024). Comparison of Optical Parameters of Transparent Metal Oxide CdO and CdAlO Thin Films Produced by Electrochemical Deposition. *The Black Sea Journal of Sciences*, 14(4), 2302-2310.

The Black Sea Journal of Sciences, 14(4), 2302-2310, 2024. DOI: 10.31466/kfbd.1559447

KFBD

Karadeniz Fen Bilimleri Dergisi
The Black Sea Journal of Sciences
ISSN (Online): 2564-7377 https://dergipark.org.tr/tr/pub/kfbd

Araştırma Makalesi / Research Article

Comparison of Optical Parameters of Transparent Metal Oxide CdO and CdAlO Thin Films Produced by Electrochemical Deposition

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Abstract

In this study, CdO and CdAlO thin films were produced using a single-step electrochemical deposition method, and their basic optical parameters were compared. Optical analysis was performed in the wavelength range of 300-700 nm. As a result of the optical analysis, it was observed that the CdAlO thin film was more transparent at higher wavelengths and had a higher absorption capacity at lower wavelengths compared to the CdO thin film. The maximum transmittance (T%) was 43% for the CdO thin film and 55% for the CdAlO thin film. At 300 nm, the reflection (R%) value of the CdO thin film was 6.5%, while the R% value of the CdAlO thin film was 7.5%. The maximum absorption coefficient (α) value of the CdO thin film was 1.9×10^6 m^{-1}, while the maximum α of the CdAlO thin film was 2.9×10^6 m^{-1}. At 300 nm, the extinction coefficient (k), refractive index (n), energy band gap (Eg), and optical conductivity (σ) values of the CdO thin film were 0.04, 1.26, 2.82 eV, and 5.9×10^{14}, respectively, while for the CdAlO thin film, these values were 0.07, 1.31, 3.11 eV, and 9.2×10^{14}, respectively. Based on these results, it was concluded that the CdAlO thin film exhibited higher values compared to the CdO thin film.

Keywords: Metal oxide, CdO, CdAlO, Optical parameter .

Elektrokimyasal Depolama ile Üretilen Transparan Metal Oksit CdO Ve CdAlO İnce Filmlerinin Optik Parametrelerinin Karşılaştırılması

Öz

Bu çalışmada tek adımda elektrokimyasal depolama yöntemiyle CdO ve CdAlO ince filmleri üretilmiş ve temel optik parametreleri kıyaslanmıştır. Optik inceleme 300-700 nm dalga boyu aralığında gerçekleştirilmiştir. Optiksel analizler sonucunda CdAlO ince filminin CdO ince filmine göre yüksek dalga boylarında daha geçirgen ve düşük dalga boylarında ise soğurma kapasitesinin yüksek olduğu görülmüştür. Maksimum geçirgenlik (T%) CdO ince filmi için 43%, CdAlO ince filmi için 55%'dir. 300 nm de CdO ince filminin yansıma (R%) değeri 6.5% iken CdAlO ince filminin R% değeri 7.5% tir. CdO ince filminin maksimum soğurma katsayısı (α) değeri 1.9×10^6 m^{-1} iken CdAlO ince filminin maksimum (α) 2.9×10^6 m^{-1} dir. 300 nm de CdO ince filmin sönüm katsayısı (k), kırılma indisi (n), enerji band aralığı (Eg) ve optiksel iletkenlik (σ) değerleri sırasıyla 0.04, 1.26, 2.82 eV ve 5.9×10^{14} iken CdAlO ince filminin bu değerleri sırasıyla 0.07, 1.31, 3.11 eV ve 9.2×10^{14}'tür. Bu sonuçlar neticesinde CdAlO ince filminin CdO ince filmine göre daha yüksek optiksel değerlere sahip olduğu görülmüştür.

Anahtar Kelimeler: Metal oksit, CdO, CdAlO, Optiksel parametre.

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Geliş/Received: 01.10.2024 **Kabul/Accepted:** 11.12.2024 **Yayın/Published:** 15.12.2024

1. Introduction

In recent years, there has been a lot of effort on the manufacturing and analysis of the physical characteristics of transparent conducting oxide (TCO) materials because they have fascinating optical features such as high optical transmittance(Aktas, 2023; Béaur et al., 2013; Chua, Xu, Ren, Cheng, & Ostrikov, 2009; R. K. Gupta, Ghosh, Mishra, & Kahol, 2008; R. K. Gupta, Ghosh, Patel, Mishra, & Kahol, 2009; İlhan, Gorunmez Gungor, Koc, Coşkun, & Yakuphanoğlu, 2023; Unal, 2023; Upadhyay, Kumar, & Purohit, 2021). TCO's such as ITO, MgO, CdO, ZnO, NiO, CuO are widely used as transparent electrodes in optoelectronic devices, solar cells, biosensing technology and gas sensor applications (Aydın & Sezgintürk, 2017; Chandiramouli & Jeyaprakash, 2013; Raj, Jayachandran, & Sanjeeviraja, 2010; Samarasekara, Kumara, & Yapa, 2006; Ukoba, Eloka-Eboka, & Inambao, 2018; Znaidi, 2010). CdO, one of the TCOs, is a potential material for a variety of applications due to its excellent electrical conductivity and optical transmittance in the visible sun spectrum. On the other hand, it displays a straight band gap in the region of 2.2-2.8eV (Yang et al., 2006). The basic characteristic parameters of pure CdO thin films are usually controlled by doping with different metallic ions such as In, Ga, Al, Co, Ni, Cu (Dakhel, 2014; Ram K Gupta, Ghosh, Patel, Mishra, & Kahol, 2008; Thambidurai, Muthukumarasamy, Ranjitha, & Velauthapillai, 2015; Velusamy et al., 2018; Wongcharoen, Gaewdang, & Wongcharoen, 2012; Yakuphanoglu, 2011).

CdO and doped CdO thin films can be produced using chemical bath deposition, metal organic chemical vapor deposition, pulsed laser deposition, DC magnetron sputtering methods (de León-Gutiérrez et al., 2006; Lamb & Irvine, 2009; Subramanyam, Uthanna, & Naidu, 1998). However, unlike these methods, simple, cheap, easy-to-control electrochemical deposition methods that do not require expensive equipment can also be used (Fatih, 2023).

Generally, low doping percentages are favored while doping. In this work, however, we generated both CdO and CdAlO thin films utilizing equal ratios of Cd and Al precursors via electrochemical deposition and examined their fundamental optical properties.

2. Materials and Methods

CdO and CdAlO thin films were produced on an ITO/glass substrate of 2x1 cm in size using a single-step electrochemical deposition method. Before the substrate coating process, it was cleaned in an ultrasonic bath for 10 minutes each with detergent, acetone, and propanol, and then dried with nitrogen gas. The substrates were masked so that the coating process was performed only on a 1x1 cm area. Ag/AgCl was used as the reference electrode, and a 2x1 cm Pt plate was used as the counter electrode. A 5 mM $Cd(NO_2)_3.4H_2O$ solution was used as the Cd source, and a 5 mM $Al(NO_3)_3{\cdot}9H_2O$

solution was used as the Al source. A 250 mM LiCl solution was used as the supporting electrolyte. The application temperature was set to 70°C, the applied potential was -0.7 V, and the application time was set to 3600 seconds. The coating process was performed using the Metrohm Autolab PGSTAT128N, and optical analysis was conducted using a Hach DR600 model UV-Vis spectrometer.

3. Findings and Discussion

To determine the optical properties of CdO and CdAlO thin films, the absorption spectrum of the films was recorded in the wavelength range of 300-700 nm, and other optical parameters were calculated from this spectrum. Figure 1a shows the absorption spectrum of CdO and CdAlO thin films as a function of wavelength. As the wavelength increased, the absorption capacity of both thin films decreased, with maximum absorption occurring at 300 nm. While an absorption shoulder was observed in the 376-387 nm wavelength range for the CdO thin film, a shoulder peak was seen in the 368-370 nm wavelength range. It was observed that the CdAlO thin film exhibited higher absorption at lower wavelengths, whereas the CdO thin film exhibited higher absorption at higher wavelengths. This can be explained by the increased absorption of free carriers due to the presence of Al atoms (Gencer Imer, 2016).

Figure 1b shows the transmittance (*T*) values of CdO and CdAlO thin films against wavelength. The *T* is determined by the following equation 1 (Aktas et al., 2023).

$$A = -logT \tag{1}$$

Here, *A* represents absorption, and *T* represents transmittance. The maximum *T%* value for both thin films was observed at 700 nm. At 700 nm, the *T%* of the CdO and CdAlO thin films are 43% and 55%, respectively. The lowest *T%* were observed at 300 nm, where absorption was at its maximum. These values are 37% for the CdO thin film and 22% for the CdAlO thin film. It was observed that the CdO thin film exhibited a more stable transmittance behavior against wavelength variation. At lower wavelengths, the CdO thin film was more transparent, while at higher wavelengths, the CdAlO thin film was more transparent. This can be explained by the higher absorption spectrum (R. K. Gupta, Serbetçi, & Yakuphanoglu, 2012).

In Figure 1c, the reflectance values (*R*) of CdO and CdO thin films are given against wavelength. The *R* is determined by the following equation 2(Pankove, 1975).

$$R = 1 - \left(\frac{T}{\exp(-A)}\right)^{1/2} \tag{2}$$

Here, R represents reflection, A represents absorption, and T represents transmittance. As the wavelength increased, the $R\%$ decreased for both thin films. At 300 nm, the $R\%$ value of the CdO thin film was 6.5%, while the $R\%$ value of the CdAlO thin film was 7.5%, and at 700 nm, these values decreased to 6.1 and 5.3, respectively. These differences between the films may be due to differences in the grain sizes of the CdO and CdAlO thin films (R. K. Gupta et al., 2012).

Figure 1d shows the absorption coefficient (α) values of CdO and CdO thin films versus wavelength. The α is given by the following equation 3 (Tüzemen, Eker, Kavak, & Esen, 2009).

$$\alpha = \frac{2.303 \cdot A}{t} \tag{3}$$

Here, A represents absorption, and t represents thickness (approximately 500 nm). For both films, the absorption coefficient values decreased as the wavelength increased, and the maximum absorption coefficient values were observed at 300 nm. The maximum α value of the CdO thin film was 1.9×10^6 m^{-1}, while the maximum α of the CdAlO thin film was 2.9×10^6 m^{-1}. The presence of Al atoms increased the absorption capacity.

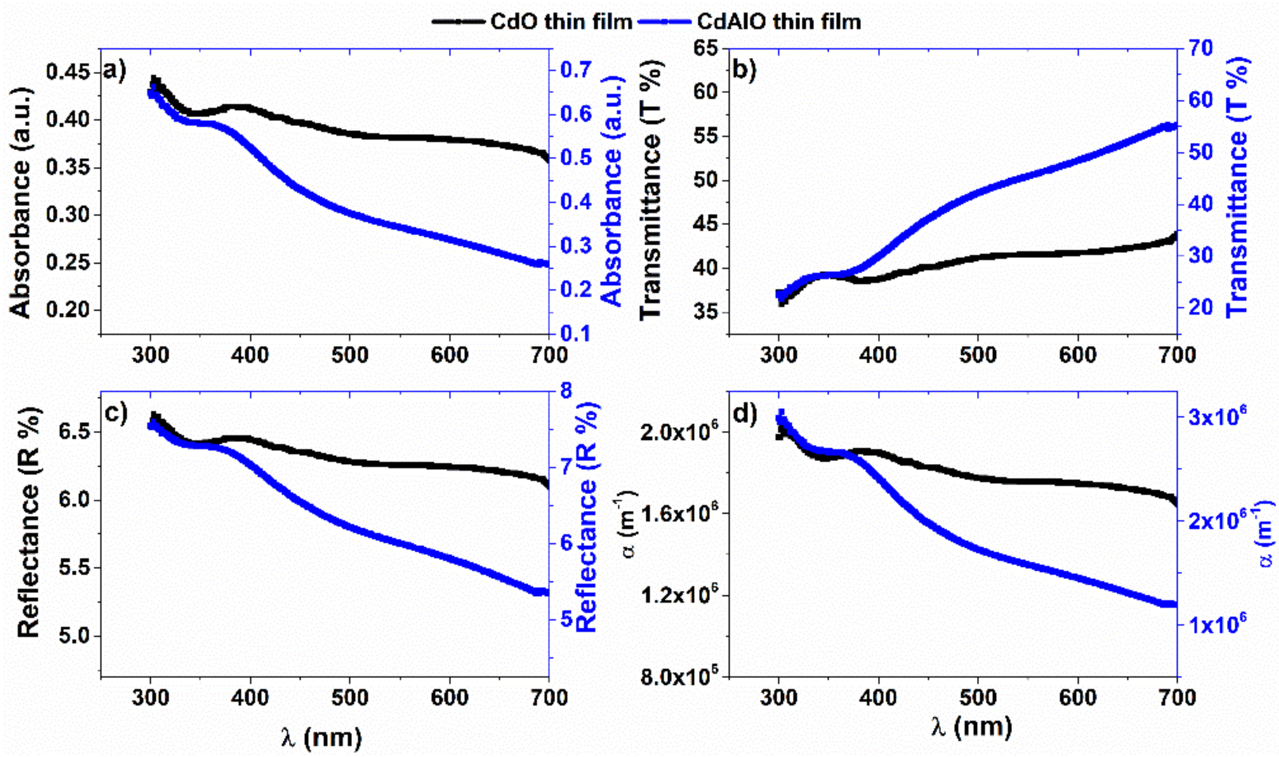

Figure 1. Variation of a) Absorbance (A), b) Transmittance ($T\%$), c) Reflecttance ($R\%$) and d) Absorption coefficient (α) versus wavelength of CdO and CdAlO thin films.

Figure 2a shows the variation of the extinction coefficient (*k*) values of CdO and CdAlO thin films as a function of wavelength. The *k* is given by the following equation 4 (Benramdane, Murad, Misho, Ziane, & Kebbab, 1997).

$$k = \frac{\lambda \cdot \alpha}{4\pi} \tag{4}$$

where *k* is the extinction coefficient, λ is the wavelength of the incident light, and α is the absorption coefficient. The *k* value of the CdO thin film increased as the wavelength increased, while the change in the CdAlO thin film was irregular. At 700 nm, the *k* value of the CdO thin film was 0.09, while the *k* value of the CdAlO thin film was 0.06. At 300 nm, the *k* value of the CdO thin film was 0.04, and the *k* value of the CdAlO thin film was 0.07. The maximum *k* value was observed at 700 nm for the CdO thin film, while for the CdAlO thin film, it was observed at 383 nm. Additionally, the *k* value showed a shoulder peak at 592 nm.

Figure 2b shows the variation of the refractive index (*n*) values of CdO and CdAlO thin films as a function of wavelength. The *n* is given by the following equation 5 (Benramdane et al., 1997; Kose, Atay, Bilgin, & Akyuz, 2009).

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{1-R^2} - k^2} \tag{5}$$

where *n* is the refractive index, *R* is reflectance, and *k* is the extinction coefficient. The *n* values for both thin films decreased as the wavelength increased, and the maximum *n* values were observed at 300 nm. At 300 nm, the *n* value of the CdO thin film was 1.26, while the *n* value of the CdAlO thin film was 1.31. At 700 nm, these values were 1.24 and 1.21, respectively. At lower wavelengths, the *n* values of the CdAlO thin film were higher than those of the CdO thin film, while at higher wavelengths, this situation was reversed.

Figure 2c shows the plot of $(\alpha h\nu)^2$ against $h\nu$ for determining the energy band gaps (*Eg*) of CdO and CdAlO thin films. The relationship between α and *Eg* is given by the equation 6 (Tauc, Grigorovici, & Vancu, 1966).

$$\alpha(h\upsilon) \approx \left(h\upsilon - E_g\right)^n \tag{6}$$

where $h\upsilon$ is photon energy and *n* is ½ for direct allowed transitions. From the plots of $(\alpha h\upsilon)^{\frac{1}{n}}$ versus hυ, *Eg* is determined with the extrapolation of the straight line portion of the plot to the energy axis. Then the intercept gives the value of *Eg* (Dwivedi, Dayashankar, Singh, & Dubey, 2010)

The *Eg* value of the CdO thin film was 2.82 eV, while the *Eg* value of the CdAlO thin film was 3.11 eV. Quantum confinement in semiconductor clusters provides an alternative and more fundamental explanation for the band gap variation in nanostructured materials (Inamdar, Sonavane, Sharma, Im, & Patil, 2010). The possible reason for this change in the optical band gap could be due to variations in the grain size of the films. It has been reported that quantum confinement contributes to the widening of the band gap in small grain sizes (Green & Hussain, 1991).

Figure 2d shows the variation of the optical conductivity (*σ*) values of CdO and CdAlO thin films as a function of wavelength. The σ is given by the following equation 7 (Kurt, Aktas, Ünal, & Kabaer, 2022).

$$\sigma = \alpha nc/4\pi \tag{7}$$

where *α* is the absorption coefficient, *n* is the refractive index, and *c* is the speed of light. The *σ* values for both films decreased as the wavelength increased. The maximum *σ* value was observed at 300 nm, with a value of 5.9×10^{14} for the CdO thin film and 9.2×10^{14} for the CdAlO thin film. At 700 nm, the *σ* values were 4.84×10^{14} and 3.40×10^{14}, respectively. At smaller wavelengths, the *σ* value of the CdAlO thin film was higher, while at larger wavelengths, the *σ* value of the CdO thin film was greater.

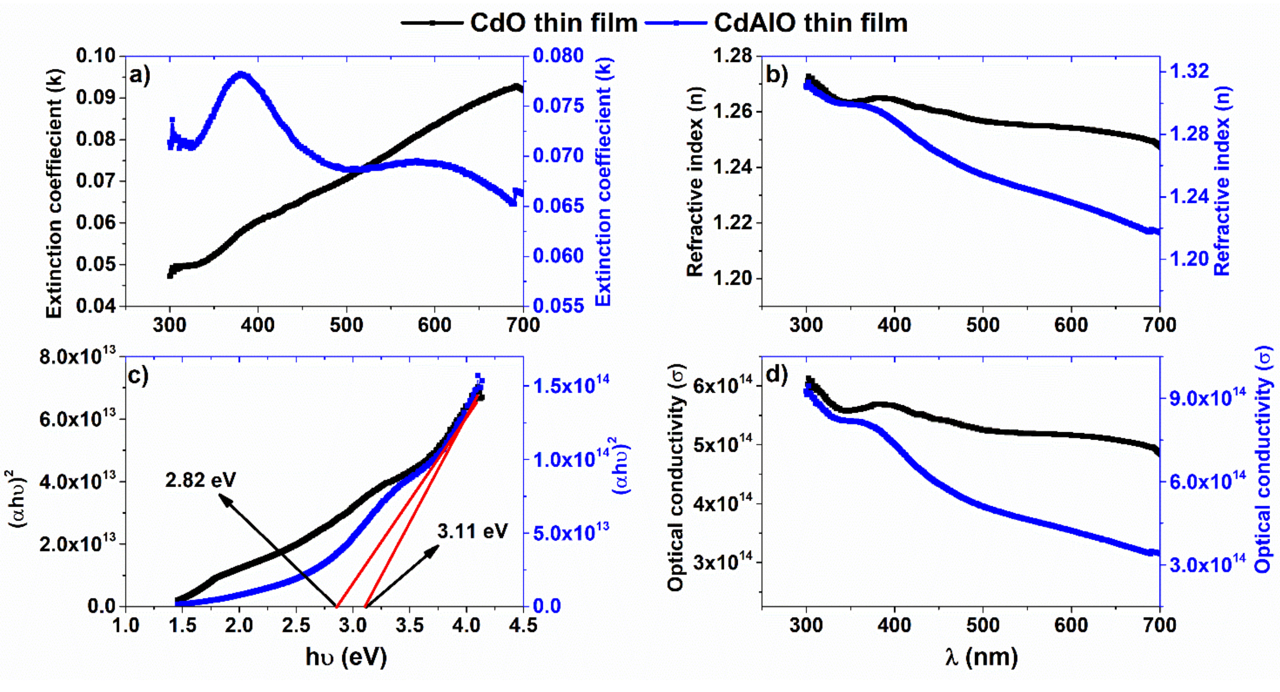

Figure 2. a) Extinction coefficient (*k*), b) Refractive index (*n*), c) *(αhυ)²* versus *hυ* and d) Optical conductivity (*σ*) variation versus wavelength of CdO and CdAlO thin films.

4. Conclusions and Recommendations

CdO and CdAlO thin films were successfully produced using a single-step electrochemical deposition method. The basic optical parameters were thoroughly investigated and compared in the wavelength range of 300-700 nm. The presence of Al atoms increased the forbidden energy band gap and the absorption capacity at 300 nm. Additionally, both the optical conductivity and the extinction coefficient, as well as the refractive index values, increased in the absorption region.

Acknowledgements

A part of this study was supported by Giresun University Scientific Research Projects Coordinatorship with project number FEN-BAP-A-290224-53.

Authors' Contributions

The study has a single author

Statement of Conflicts of Interest

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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