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Ultrasonik kimyasal püskürtme tekniği ile depolanan ve tavlanan CdO filmleri arasındaki optik, elektrik ve yüzey farklılıkları

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ÖZET

Kadmiyum oksit (CdO) filmleri taban sıcaklığı 300 °C olan cam tabanlar üzerine ultrasonik kimyasal püskürtme tekniği kullanılarak elde edilmiştir ve daha sonra 500 °C'deki hava ortamında tavlanmıştır. CdO filmlerinin bazı fiziksel özellikleri, optik geçirgenlik, soğurma, dört uç metodu ve atomik kuvvet mikroskobu farklı teknikler kullanılarak belirlenmiştir. Ayrıca filmlerin optik, elektrik ve yüzey özellikleri üzerine tavlama işleminin etkisi araştırılmıştır.

Anahtar Kelimeler: Kadmiyum oksit, ultrasonik kimyasal püskürtme tekniği, tavlama, atomik kuvvet mikroskobu.

The optical, electrical and surface differences between as-deposited and annealed CdO films deposited by ultrasonic spray pyrolysis

ABSTRACT

The cadmium oxide (CdO) films were deposited by ultrasonic spray pyrolysis technique on glass substrates at 300 °C and subsequently annealed at higher temperature up to 500 °C in air ambient. Some physical properties of CdO films were characterized using different techniques such as optical transmittance, absorbance, four probe method, and atomic force microscopy. Also, the effect of annealing on the optical, electrical and surface properties of films was investigated.

Keywords: Cadmium oxide, ultrasonic spray pyrolysis technique, annealing, atomic force microscopy.

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1. INTRODUCTION

CdO films which are material belongs to Transparent Conducting Oxide (TCO) family were used common application area such as photovoltaic solar cells, optoelectronic devices and gas sensors [1-3]. CdO is an important semiconducting material with a high electrical conductivity and high optical transmittance. Also, CdO is an n-type semiconductor with a band gap changing in the range of 2.2–2.8 eV and possesses low resistivity (10^{-2} to 10^{-4} Ω.cm) due to the defect of oxygen vacancies and cadmium interstitials [4-6].

CdO films have been prepared by various chemical and physical deposition techniques such as spray pyrolysis [7, 8], chemical bath deposition [9], electrodeposition [10-14], metal organic chemical vapor deposition (MOCVD) [15], sol–gel [16,17], pulsed laser deposition [18,19], magnetron sputtering [20,21] and RF sputtering [22]. In this work, we have employed ultrasonic spray pyrolyis method to prepare CdO films because of its very easy to handle and cost effective as well. This article reports the optical, electrical, and surface properties of as-deposited and annealed CdO films produced using ultrasonic spray pyrolysis technique.

2. EXPERIMENTAL

The CdO film was deposited on glass substrates by spray pyrolysis technique using a homemade experimental setup shown in Figure 1. Before deposition, the microscopic glass substrates were first cleaned by acetone, then with soap and at last copiously rinsed with distilled water. Finally they were dried. The spraying solution was prepared by mixing the appropriate volumes of 0.1 M cadmium acetate $Cd(CH_3COO)_2.2H_2O$ dissolved in a mixture of deionized water and methanol (1:1). The temperature was measured by thermocouple fixed on the hot plate. During the film deposition the substrate temperature was kept constant at around 300 ± 5 °C. Air was employed as the carrier gas. CdO film deposited at 300 ± 5 °C and annealed at 500 °C during 2 h. As-deposited and annealed films are denoted by C300 and C500, where numbers stand for temperatures. The preparative conditions are tabulated in Table 1.

The thickness of CdO film is determined using filmetrics thin film measurement system. The optical transmittance and absorbance of the film were recorded in the wavelength range from 300 to 900 nm using Schimadzu UV-2550 UV-VIS double beam spectrophotometer. The room temperature resistivity of CdO film was measured using Keithley 2601A System Source Meter Four-probe set up. Also, surface properties were carried out using Park System XE 70 model -AFM atomic force microscopy.

Table 1. Preparative parameters for CdO film

No	Parameter	Specification
1	Substrate temperature (°C)	300 ± 5
2	Carrier gas, Pressure of carrier gas (bar)	Air, 1
3	Nozzle to substrate distance (cm)	30
4	Total spray time (min)	30
5	Solution flow rate (mL/ min)	5
6	Annealing temperature (°C)	500
7	Annealing time (h)	2
8	As-deposited CdO	C300
9	Annealed CdO	C500

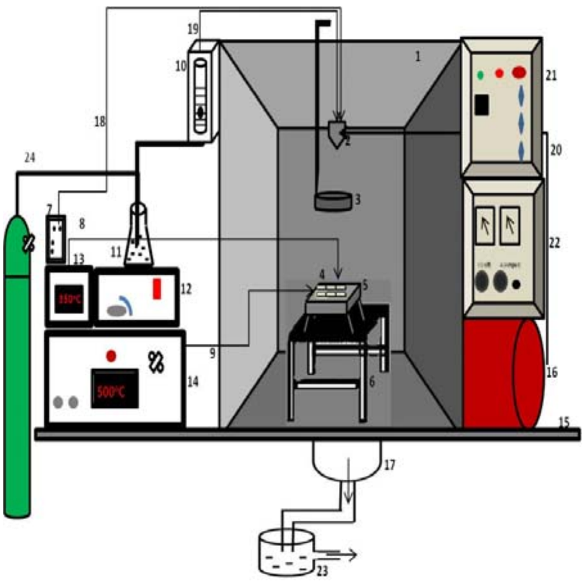

Figure 1. (1) Spraying chamber, (2) Ultrasonic atomizer, (3) Moving pan (4) Glass substrates (5) Bronze block (5000-6000 Watt), (6) Moving base, (7) Oscillator, (8) 1. termocouple, (9) 2. termocouple, (10) Flowmeter, (11) Spraying solution, (12) Heater-magnetic mixer, (13) Temperature indicator, (14) Electrical heater, (15) Table, (16) Air gas, (17) Fan, (18) Cable of oscillator, (19) Spraying hose, (20) Air hose, (21) ac ampermeter (22) ac voltmeter, (23) water-filled container (24) N_2 tube

3. RESULT and DISCUSSION

The optical properties of the prepared film on glass substrates were studied by a method of optical transmission. The optical transmittance and absorbance curves as a function of wavelength are plotted in Figs. 2 (a) and (b). It has been found that the absorption increases abruptly with the decrease in wavelength. Also, it is shown that absorbance decreases with annealing and a sharp decrease is observed near the band edge.

The transmittance spectra of CdO thin film is expected to depend mainly on three factors (1) oxygen deficiency, (2) surface roughness and (3) impurity centers. The transmission spectrum of CdO film was measured to investigate the effect of annealing temperature and ambient. Optical transmittance spectra of as-deposited and annealed CdO film were measured in the range of 400–800 nm at room temperature. All films show very similar optical transmissions in the 550–800 nm range, and the difference becomes more pronounced at shorter wavelengths. The optical band edge shifts to higher wavelength with annealing. In the visible region of the spectrum, the transmittance of annealed film was found to vary from about 50 % to 60 % depending on the annealing temperature and annealing ambient. The ability of a material to absorb light is measured by its absorption coefficient. The variation of the optical absorbance with wavelength is shown in Fig. 3. The calculated values of absorption coefficient are in the order of 10^3 cm^{-1}. Besides, it is observed that absorption coefficient increased with annealing. This variation could be related to the variation of the crystallinity and carrier concentration of CdO film with annealing.

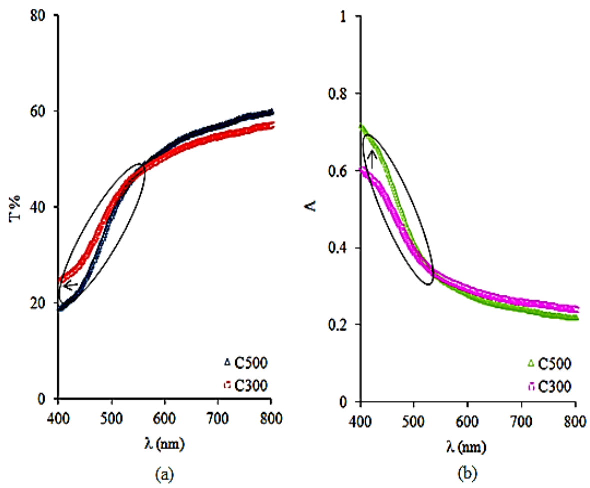

Figure 2. (a) The transmittance and (b) absorbance spectra of CdO film

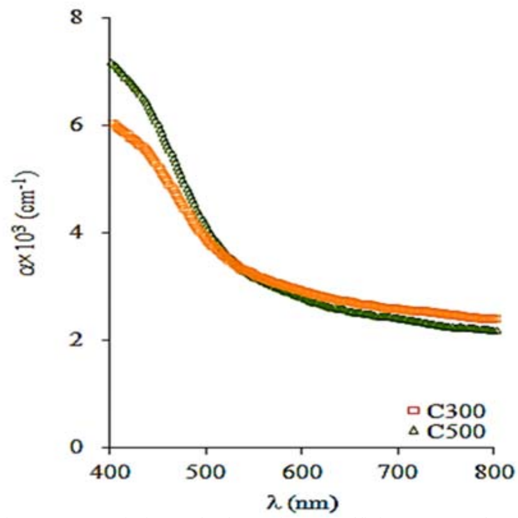

Figure 3. Variation of absorption coefficient as a function of wavelength

The optical transition type and the band gap E_g can be determined using equation:

$$\alpha=A\,(h\nu-E_g)^n \quad (1)$$

where α is the absorption coefficient, A is a constant and hν is the photon energy. For direct and indirect transitions n is equal to 1/2 and 2 values, respectively. The $(\alpha h\nu)^2$ versus hν plot (Fig. 4) is linear in nature at the absorption edge, confirming that the material of the film has a direct band gap. Energy band gaps of as-deposited and annealed CdO films were obtained by extrapolating the linear part of the curve $(\alpha h\nu)^2$ versus hν and the results is shown in Fig. 4.

It is seen that direct optical band gap of CdO film decreased from 2.44 eV to 2.26 eV with annealing at 500 °C. It is clear that, the micro-structure behavior has importance upon the optical properties of this film [23]. This change in the optical band gap may be attributed to the change in crystallinity of the film since grain size changes with annealing. The decrease in the carrier concentration may be originated from the appearing point defects and interstitial impurities during the heat treatment [24].

The band gaps of the film are in good agreement with the literature, and the film has direct band transitions which is an important characteristic for photovoltaic applications. These results are similar to that observed for other annealed CdO film [23, 25-27].

The thicknesses of as-deposited and annealing CdO film are examined using filmetrics thin film measurement system. Thicknesses of the as-deposited and annealed films are 245 nm and 250 nm, respectively. AFM scans of the surface were carried out to study the change in the surface morphology of the film. AFM images of as-deposited and annealed CdO films are shown in Fig. 5. The 5 µm × 5 µm images are utilized for measuring the surface roughness of the film. The scanning frequency was set at 1 Hz. Also, R_q (root mean square), R_a (average) and R_{pv} (peak-to-valley height) roughness values of the film was examined. The roughness values of the as-deposited and annealed CdO films are shown in Table 2. It was seen that the roughness values of the film slightly decreases with the annealing. This decrease is manly related to the surface combination and surface form. The AFM images are shown clearly the influences of the annealing on the morphology of the film. CdO film shows granular surface properties. The annealed CdO film shows smooth surface compared to the as-deposited CdO film. Consequently; the surface topography of the CdO film annealed at 2 hours has the best of smooth structure. Besides, the surface combination of the CdO film may be clear away with the annealing process.

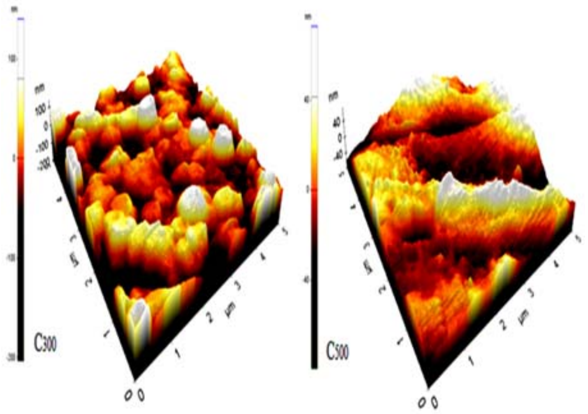

Figure 5. AFM images of CdO films

Table 2. Roughness values of CdO films

Film	R_q (nm)	R_a (nm)	R_{pv} (nm)
C300	40	31	344
C500	21	16	152

The measured values of the resistivity are shown in Table 3. It is found that the resistivity decreases with annealing. These values are in agreement with the literature [23]. We think that this change is due to the decreasing oxygen deficiencies because of the micro structural compositional change of the grains, in addition to other phenomena such as disorder and defects at the grain-boundaries. Also, when CdO film is annealed at the higher temperatures, atoms can diffuse into substitution positions in the crystal lattice. As a result, this drastic changes cause in the electrical properties of the CdO film. Also, results from the hot point probe showed that CdO film has n-type conductivity behavior.

Table 3. Electrical resistivity values of CdO films

Film	Resistiviy (Ω.cm)
C300	4.72×10^3
C500	2.48×10^3

4. CONCLUSION

In this paper, we report the preparation and characterization of CdO and annealed CdO alloy film. This film has been deposited on glass substrates by ultrasonic spray pyrolysis technique. The optical transmittance of the film was increased from 50 to 60 % and the maximum transmittance was achieved in air annealed samples. Optical band gap of the film decreased from 2.44 to 2.26 eV with annealing. This suggested that the optical band gap for CdO film was strongly dependent on the annealing process. The surface of the CdO film has changed from small granular texture to smooth texture by annealing. There is an advantage of annealed sample in order to having a little lower roughness value as compared to the as-deposited one. The increase in transparency and shift of the band gap to the higher energy values and decrease in resistivity make annealed CdO film a potential candidate for the window material in solar cell applications.

After all investigations, thermal annealing confirmed positive improvements on the physical properties of the CdO film. We think that annealed samples will improve the characteristics of optoelectronic devices.

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