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Controlling of optical band gap of the CdO films by zinc oxide

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In this study, CdZnO films prepared at different ratios of dopants (CdO:ZnO = 5:5, CdO:ZnO = 6:4, and CdO:ZnO = 8:2) were coated on glass surface by using the sol-gel spin coating technique. After this process, surface structure and optical properties of the CdZnO films was investigated by atomic force microscopy (AFM) and UV-Vis spectroscopy. The surface structure of the CdZnO films depended on the content of ZnO and CdO in the films. Low percentage of CdO films were very similar to the ZnO film but higher amount of CdO resuted in granular structures together with pure structure of ZnO in the films. Eg values of produced CdZnOs depended on the additions of CdO and ZnO. The obtained Eg values of the produced CdO:ZnO = 5:5 (S3), CdO:ZnO = 6:4 (S4), and CdO:ZnO = 8:2 (S5) films are 2.5 eV, 2.49 eV, and 2.4 eV, respectively.

Keywords: *thin film; spin coating; ZnO; CdO; optical properties*

1. Introduction

Indium oxide, tin oxide, cadmium oxide, and zinc oxide are transparent conductive films. These films have semimetallic electrical conductivity and high optical transparency in the visible region [1]. Transparent conducting oxides are very important for many applications such as solar cells, phototransistor, diodes, and sensor [2–4] as well as flat panel displays, surface acoustic wave devices, transparent conducting electrodes, and optical communications. These applications require excellent optical and electrical properties. CdO thin films can be produced using different methods. These methods include spray pyrolysis, sol-gel, chemical bath deposition, [1–5] DC magnetron sputtering [1, 6] and radio frequency sputtering. CdO has a built-in direct band gap of 2.50 eV and is not a popular TCO material because of its n type conductivity and relatively small optical band gap [1]. CdO functions as a donor in crystal structures and has a high n-type conductivity and a high electron mobility. This is an important parameter in the transparent conductivity of CdO [7].

Ions such as Al, Cu, Sn, and In are metallic ions, which can excite the structure, to control the optical properties of CdO films [1]. II-VI group semiconductors have attracted attention of researchers over the last few years. Due to their wide band gap, they find applications in light emitting diodes (LEDs) and laser diodes. Among the semiconductors, ZnO has a wide band gap (3.37 eV) and also a large exciton binding energy (60 meV). These features are significant for the use in optoelectronic devices in violet and blue areas. ZnO thin films are very important for devices emitting short wavelength light [8, 9], field emission devices [3, 8], solar cells, and sensors [8]. Their conductivities depend on oxygen vacancies and/or Zn–Cd transition when both ZnO and CdO are doped [2].

The sol-gel technique is interesting due to good optical properties, good homogeneity, ease of composition control, low equipment cost, low process temperature, and large area coverageof fabricated layers. The sol-gel technique is particularly effective in thin film production and also transparent multicomponent oxide layers of compositions on a variety of substrates including glass [8]. Maiti et al., [11] reported randomly oriented Cd-doped ZnO films containing nano bars which were prepared in various lengths. Thirumoorthi et al., [12] produced transparent conductive Sn-doped CdO thin films by using sol-gel spin coating technique. They explained a blue change of the energy gap between 2.42 eV and 2.96 eV based on the Burstein-moss

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effect. Ziabari et al., [13] produced Al-doped CdO thin films by using different sol-gel methods at different Al concentrations and indicated that all films had a smooth and spherical grain size depending on the Al content. Verma et al., [14] tempered Mg doped films and examined their optical and morphological properties. The band gap of the films increased with Mg addition. Mia et al., [15] observed a nonlinear relationship between Mg content and the optical and structural parameters by producing Mg-doped ZnO thin films. Huang et al. [16] found that the band gap energy of CdO grains with the size of less than 15.9 nm decreased and the red shift effect was observed; whereas, the band gap energy of CdO grains with the size greater than 15.9 nm increased. Dahnoun et al., [17] obtained crystalls with the size ranging from 23 nm to 47 nm and the transmittance of 80 % in the ZnO films they produced. Khan et al. [18] achieved a transmittance of 80 % in multi-layer ZnO films and observed that the multilayers showed better transparent conductive performance than single-layer ZnO. Patil et al., [19] evaluated the gas sensing performance of ZnO film produced at different temperatures. ZnO film sensor showed a high stability and a moderate response and recovery time for NO_2 gas. Chavan et al., [20] studied the effects of annealing temperature, aging time and speed of rotation on surface roughness and crystal size in ZnO thin films. Alahmed et al., [21] controlled the particle size with Mn in the Mn-doped CdO films. They stated that the Eg values increased with an increase in Mn content. Turgut et al., [22] determined that in CdO films produced by sol-gel method, the amount of Sc addition affected the optical band gap, lattice constant, crystal size, and layer resistance of CdO. Aydemir et al., [23] found that in Al-doped CdO films, a decrease in Eg values was associated with structural modification and the intensity of these defects was dependent on the intensity of the situation.

In this study, CdZnO thin films were coated on glass substrates by using sol-gel spin coating technique at different rates. Then, the characterizations of these coatings were performed. The purpose of this study was to determine the effect of different compositions on the optical properties of obtained films.

2. Experimental

CdO, ZnO and CdZnO films were produced and deposited on glass substartes using sol-gel spin coating technique. Chemicals in the analytical reagent class were used. All of the chemicals were supplied from Alfa Aesar. Pure 0.5 M ZnO and 0.5 M CdO films were prepared using zinc acetate dihydrate and cadmium acetate dihydrate, respectively. In the study, zinc-acetate-dihydrate was dissolved in 2-methoxy-ethanol ($C_3H_8O_2$). This process was carried out in a magnetic stirrer at 70 °C at 500 rpm for 60 min. The same procedure was carried out for the cadmium acetate-dihydrate at 60 °C at 500 rpm and 60 min in a magnetic stirrer. The solution of ethanolamine was added as a sol stabilizer for a more homogeneous dispersion. CdZnO mixture was prepared at different volume ratios of Cd:ZnO = 5:5 (S3), Cd:ZnO = 6:4 (S4), and CdO:ZnO = 8:2 (S5). The solutions were also mixed at 60 °C, 500 rpm and treated for 60 min with the help of magnetic stirrer. Finally, the obtained thin films were subjected to sol-gel spin coating. The films were deposited at 1500 rpm for 30 s and then were dried at 60 °C. Coating and drying processes were repeated 8 times. Afterwards, pure and doped films were annealed at 450 °C for 60 min. The thickness of the annealed films was found to be 200 nm. Surface morphology of the films was examined using atomic force microscopy (AFM). Optical properties of the CdZnO films were investigated by UV-Vis spectroscopy.

3. Results

Fig. 1 to Fig. 4 show the surface morphologies of pure CdO (S1) and CdZnO thin films with different compositions: CdO:ZnO = 5:5 (S3), CdO:ZnO = 6:4 (S4), and CdO:ZnO = 8:2 (S5). All the images were obtained using AFM.

CdO (S1) films had only a few nanometers in size. The surface morphologies of CdZnO thin films were related to the percentages of ZnO and CdO in the composite. ZnO thin films had a wrinkled structure whereas CdO thin films had a flower-like structure. The films containing high content of CdO had a fiber structure and a flower like

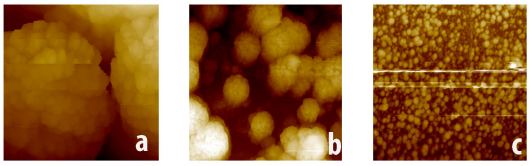

Fig. 1. S1 (CdO) a) 1×1μm, b) 5×5 μm, c) 40×40 μm.

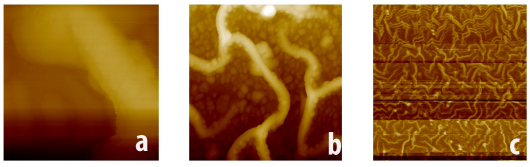

Fig. 2. S3 (Cd:ZnO = 5:5) a) 1×1 μm, b) 5×5 μm, c) 40×40 μm.

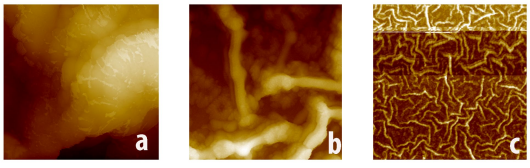

Fig. 3. S4 (Cd:ZnO = 6:4) a) 1×1 μm, b) 5×5 μm, c) 40×40 μm.

grain due to the own morphological structure of ZnO. On the other hand, the films containing low CdO had a fiber-like structure such as the pure ZnO films. CdZnO films produced by the sol-gel method showed a structure with irregular wrinkles. The reason for this structure was the compressive membrane force, which was generated by the thermal expansion coefficients difference between the substrate and the thin films during the drying process [8]. The surface of undoped ZnO was composed of nanorods, but with the addition of Cd, these nanorods were converted into nanoclusters. Depending on the CdO:ZnO ratio, the shape of the thin films varied. When the figures were examined, CdO and ZnO thin films were uniformly distributed on the surface. It was observed that the films containing ZnO and CdO in equal proportion Cd:ZnO = 5:5 (S3) had a flake-like

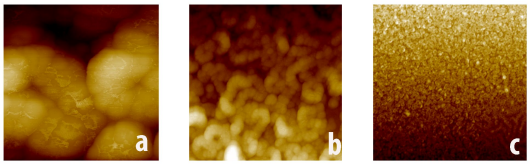

Fig. 4. S5 (CdO:ZnO = 8:2) a) 1×1 μm, b) 5×5 μm, c) 40×40 μm.

morphology. In the films with high amount of CdO, CdO:ZnO = 8:2 (S5), the cauliflower structures were formed. Fig. 4 shows small grain on and between the large grains. Due to the difference in the radius between the elements Zn and Cd, the lattice distortion occurred. The size of the crystal might be reduced due to this lattice distortion. Oxygen vacancies also played an important role in the structure and caused small crystal sizes [24].

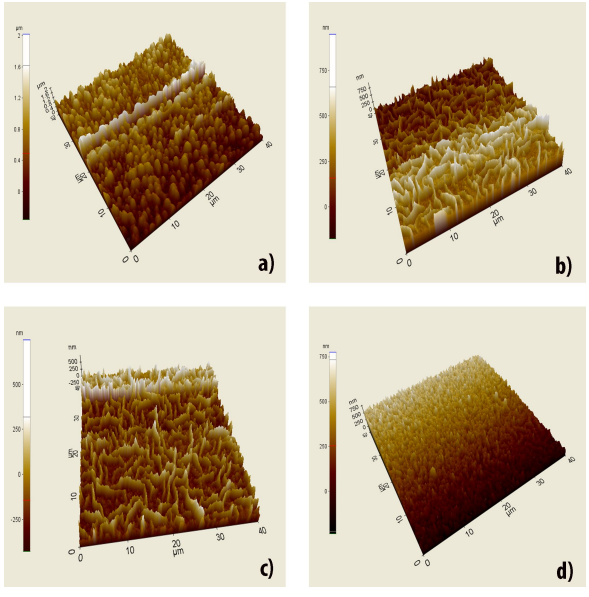

Fig. 5. AFM topografic images (40×40 μm).

Fig. 5 shows the differences in roughness and microstructure of the CdZnO films observed in AFM measurements. While the surface roughness value of pure CdO was 226 nm, the prepared surface roughness values were found to be 90 nm, 125 nm, and 66 nm for S3, S4, and S5, respectively. The surface roughness of the samples not only gave information about light scattering but also showed

the quality of the investigated surface. The average grain size was about 860 nm for pure CdO. The fiber thickness of sample S3 was 430 nm, the fiber thickness of sample S4 was 378 nm, and the grain size of sample S5 was 312 nm. The samples with higher concentrations of Cd had reduced in grain size. The grain size and the surface roughness decreased. The surface properties of all samples were found to be almost identical. Only the grain size and roughness varied depending on the ratio of both oxides [2]. As the ratio of Cd increased, better crystallization was observed.

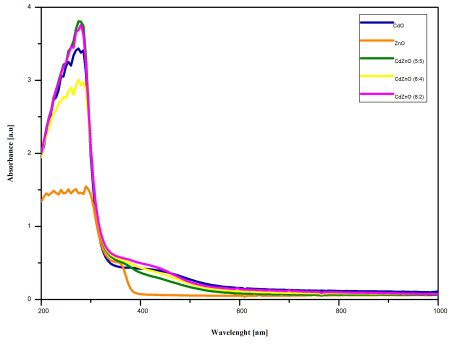

Fig. 6. Absorption spectra of CdO, ZnO, CdOZnO = 5:5, CdOZnO = 6:4, CdOZnO = 8:2 films.

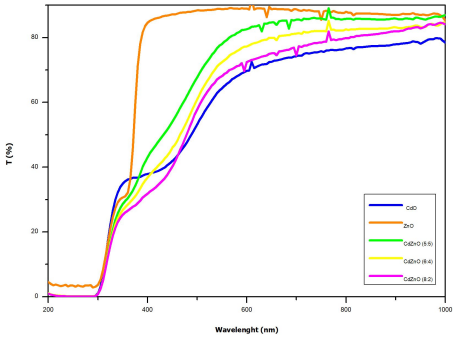

Fig. 7. Transmittance spectra of CdO, ZnO, CdOZnO = 5:5, CdOZnO = 6:4, CdOZnO = 8 films.

Optical properties of a material are determined by its light absorption and response

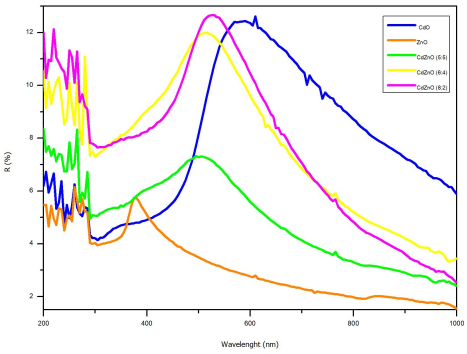

Fig. 8. Reflectance spectra of CdO, ZnO, CdOZnO = 5:5, CdOZnO = 6:4, CdOZnO = 8 films.

to electromagnetic radiation [25]. The optical values of the CdZnO thin films were investigated. Fig. 6, Fig. 7 and Fig. 8 show absorbance, transmittance and reflectance spectra, respectively as a function of wavelength with for the studied thin film. Fig. 7 shows the transmittance spectra in the wavelength range of 200 nm to 1000 nm of thin films prepared at different ratios. While the optical transmittance of CdO was about 65 %, the optical transmittance of ZnO was about 80 %. As seen from the graph, the content of CdO decreased with increasing transmittance. There were two reasons for this behavior. The first reason was that the surface roughness of the films increased due to Cd addition and the second reason was the increase in incident light optical scattering on the film surface due to the roughness of the surface. In another study, the decrease in transmittance with increasing amount of Cd was attributed to the narrowing in the band gap and free electron absorption [26]. Materials that can transmit light at low absorption and reflection are transparent materials. If the light is scattered, these materials are semi-transparent materials [25]. Metals can absorb the full frequency of visible light because of empty electron states in the material that allows electron transitions [25].

The optical band spacings of the samples were calculated based on the basic absorption, which corresponds to electron stimulation from the valence band to the transmission band [2].

In semiconductor materials, optical transitions occur indirectly or directly. The absorption coefficient for direct passages is expressed by equation 1 [27]:

$$\alpha h\nu = B(h\nu - Eg)^n \quad (1)$$

where, B is taken as a constant, α is the absorption coefficient, h is the Planck constant, Eg is the optical band gap, ν is the frequency of the incident photon and the exponent n describes the transition type [28].

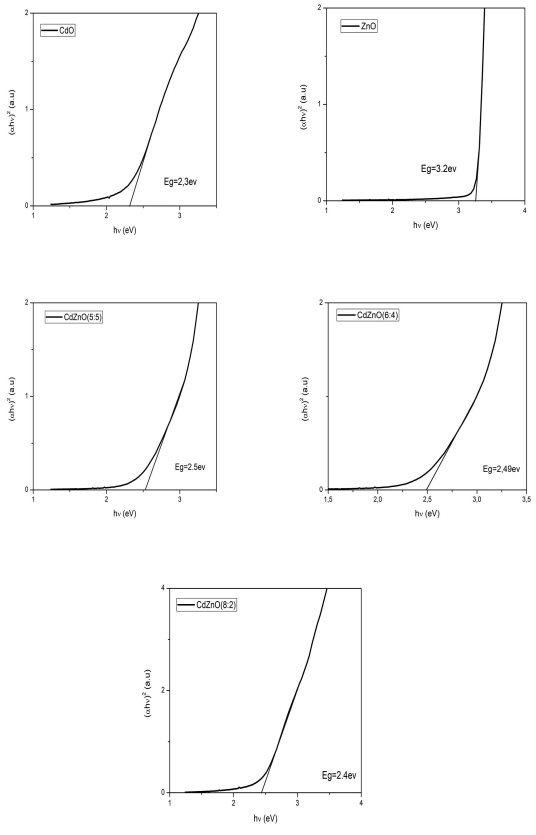

Fig. 9. Optical band gap energies of CdO, ZnO, CdOZnO = 5:5, CdOZnO = 6:4, CdOZnO = 8.

Fig. 9 shows optical band gap energies for CdO, ZnO, and CdZnO thin films. When these graphics were examined, the band gap of pure CdO was calculated as 2.3 eV; whereas, the pure ZnO band gap was calculated as 3.2 eV. Eg values of the produced samples CdO:ZnO = 5:5, Cd:ZnO = 6:4, and Cd:ZnO = 8:2 were calculated 2.5 eV, 2.49 eV, and 2.4 eV, respectively. The purpose of the bandgap in the produced samples is to provide a type of light necessary for dye reduction [28]. The change in optical band gap may contribute to the band shrinkage effect due to the increased concentration of doped material. El Sayed et al. [10], indicated that as the Cd content increased, the Eg values decreased. They explained that when ZnO was doped with Cd, the Cd^{+2} ions settled in the transition areas or uniformly substituted into the Zn^{2+} in ZnO lattice [10]. CdO had a smaller bandgap than ZnO. The narrow band gap was the element of Cd in ZnO and it did not allow new recombinations with this low emission energy [13]. Additionally, in the studies conducted by Yakuphanoğlu with Ni doped CdO thin films and by Dağdelen with Bi doped CdO thin films, they reported that Bi and Ni content increased the band gap values of CdO thin films [1]. The optical bandgaps of undoped CdO films were lower than the optical bandgaps of CdO films obtained by various methods [1]. The variation of bandgap values may also depend on the variation of strain.

4. Conclusions

CdZnO thin films at different ratios of Cd and Zn elements were successfully prepared by using sol-gel spin coating method. Structural and optical properties of the prepared samples were examined. The surface roughness values of the prepared samples were found to be 90 nm, 125 nm, and 66 nm for S3, S4, and S5, respectively. Transmitance of the samples increased with decreasing CdO content. Eg values of the produced samples CdO:ZnO = 5:5 (S3), CdO:ZnO = 6:4 (S4), and CdO:ZnO = 8:2 (S5) were calculated as 2.5 eV, 2.49 eV, and 2.4 eV, respectively. Eg values decreased as the Cd content increased.

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