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Research Article

ELABORATION AND CHARACTERIZATION OF NANOCRYSTALLINE CADMIUM OXIDE FILMS

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ABSTRACT

Cadmium oxide in thin film was deposited on glass substrates by spray pyrolysis technique from aqueous solution of cadmium nitrate. The diagrams of X-ray diffraction show that the films are polycrystalline. Morphological study shows uniform deposited film and submicron sized grains growth perpendicularly on substrate surface. Optical gap energy of cadmium oxide was estimated to be 2.15eV. Optical study shows that CdO film transmitted in visible and in the near red infrared wavelength range. The conductivity study indicates a semi-conducting behavior of cadmium oxide in thin films. Dielectric response of cadmium oxide films was interpreted by orientation and space charge polarization.

Keywords: CdO thin films; Spray pyrolysis; Morphological properties; AC conductivity; Dielectric properties.

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1. INTRODUCTION

There is been great deal of interest in cadmium oxide CdO chalcogenide thin films recently, as seen from a great number of publications. The interest in CdO is manifested and made clearly by its prospects in many applications such as the solar cells [1], ethanol sensing [2][3], gaz detector [4], photodiodes phototransistors [5] and IR detectors and antireflecting coatings [6], owing to its direct band gap varied between 2.2eV and 2.9eV at 300°K [7][8][9]. CdO crystallize in the cubic system with lattice parameter of a=4.69485 Ǻ [10]. It is an n-type semiconductor material of groups II-VI which belong to transparent conductive oxides (TCO) due to its high electrical conductivity and optical transmittance in the visible range of electromagnetic spectrum [11]. So that several divers investigations were doing to synthesize CdO in thin films using various techniques such as sol gel [12], CVD technique [13], laser ablation [14] and spray pyrolysis [15]. Indeed, there are a several technical of analyses of thin films properties, for detect and understood their behaviors.

In this work, we are particularly interested in developing CdO thin films; we have used spray pyrolysis method as one simple, inexpensive and potential technique where the preparation conditions, the solvent nature influence film properties profoundly. Not only this, we have relied on X-ray diffraction, spectrophotometer and impedance spectroscopy techniques to characterize and carrier out CdO properties.

2. RESULT AND DISCUSSION

2.1. Structural characterizations

Thin films obtained have dark yellow color; they are perfectly adhered to substrate surface. The various diffractions peak existing in X ray diffraction spectrum of CdO films, plotted on Fig. 1 prove polycrystalline nature of the material with cubic crystal structure. They are coherent with standard card 75-591 of powder. The spacing values ‘d’ calculated allows us to calculate the lattice parameter ‘a’, it is about 4.67Å; using following quadratic relation of cubic system:

$$d_{hkl} = \frac{a}{\sqrt{(h^2+k^2+l^2)}} \quad (1)$$

The crystallite size (G) is in order of 351.58 Å, it was estimated from half-width of maximum peak (200) at 2θ =38.5°, using the Sherrer formula [17]. The preferential orientation degree (P_{hkl}) of the Harris formula [18] was calculated in the angular range of 30° to 60° at most intense peak (200). $P_{(200)}$≈1: the crystallites of CdO film have a random orientation.

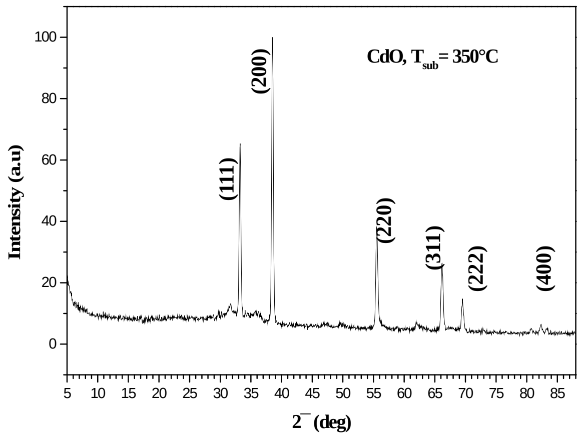
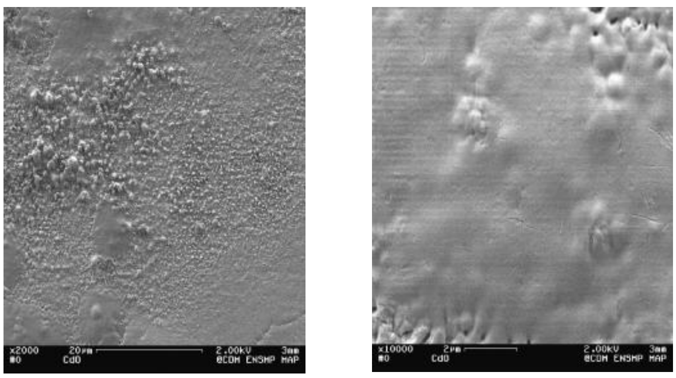


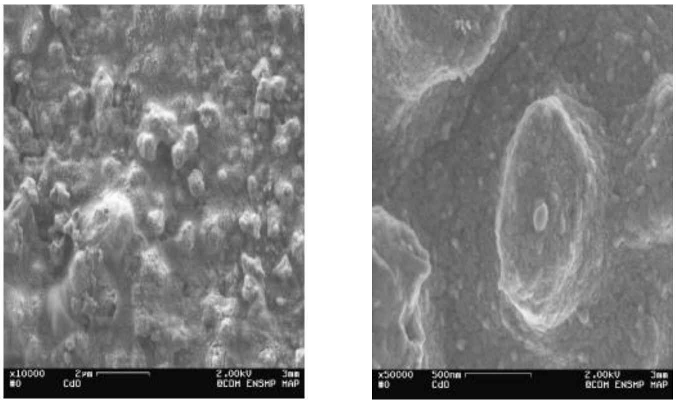
Fig.1. XRD pattern of CdO deposited at 350°c substrate temperature.

2.2. Surface morphology

Fig.2.(a), (b), (c) and (d) represent the MEB micrograph of cadmium oxide deposited at 350°c onto a glass substrate. Fig.2.(a) show relatively uniform surface with growth granular in different size. It occur uniform thin film with a smooth surface. By some side, it appear a region relatively limited on surface, it not completely occupied by the material, the crystallites are not distinguished, they are of submicron size, and it does not appear ruptures on surface of thin film. Fig.2.(b) shows the zoom on a region portion not completely devoid of the material. Fig.2.(c) display the detail of the granular region with the same zoom that Fig.2.(b). The grain growth observed makes vertically on film surface. The grains of CdO are appearing randomly formed with sizes difference on surface, this is possible do by spray technique used to deposit the films, and the supply of the material on substrate surface is not uniform. On the Fig.2.(d) obtained with the zoom of (X 50000), the grains appear under cylindrical shape with the crystallites which is growing vertically on substrate surface.



(a) **(b)**



(c) **(d)**

Fig.2. Microscopy electron beam (MEB) pictures of CdO film obtained with different zoom (a), (b), (c) and (d)

2.3. Optical properties

We operated the wavelength range of 200 to 2500 nm offered by the equipment of optical measurements to export transmission and reflexion curves of CdO films at normal incidence. In Fig. 3, optical transmission of CdO film appears very down and reduced in the short wavelengths which are due to band edge absorption. It reaches to 60% in visible wavelength range and a high average transmittance over 80% is observed in the near red infrared range. The very down of the transmittance correspond to maximum of the reflectance. From transmittance and reflectance data, absorption coefficient (α) of the film can be determined, we using following relation:

$$\boldsymbol{\alpha = \frac{1}{d}\log\left(\frac{(1-R)^2}{T}\right)} \tag{2}$$

Where d is the film thickness, in our case d is in order of the 130 nm.

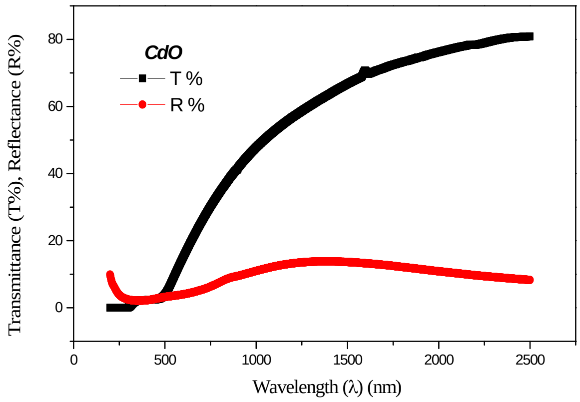


Fig.3. Transmittance (T%) and reflectance (R%) of CdO film versus the wavelength.

Fig. 4 depicts absorption coefficient (α) which is primarily due to free carriers in visible region [19]. It is of order of 10^6 cm^{-1}. (α) decreases with increases in wavelength and sharp decrease in absorption coefficient (α) was observed near band edge. This result is in good agreement with those of many works [20]. we evaluated the energy of the optical gap (*Eg*) of the film, however the values of absorption coefficient (α) calculated from the relation above were used to plot $(\alpha h\upsilon)^2$ versus (hυ) as is shown in Fig. 5, where (hυ) is the photon energy. By extrapolating linear portion of curve, direct optical gap value of the film is found to be 2.15 eV. This is a little in agreement with the intrinsic direct band gap of 2.2 eV evaluated by K. Ouari and al [7].

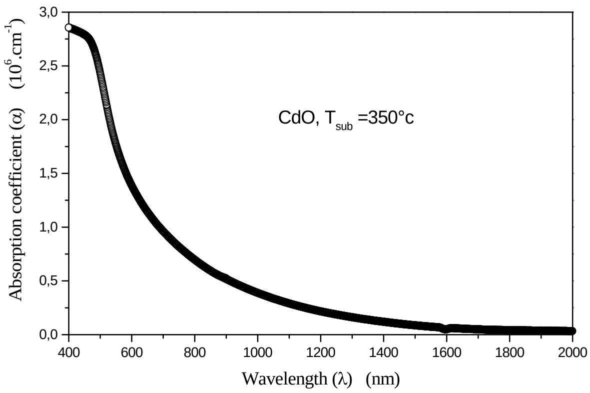


Fig.4. absorption coefficient (α) of CdO film versus the wavelength (λ).

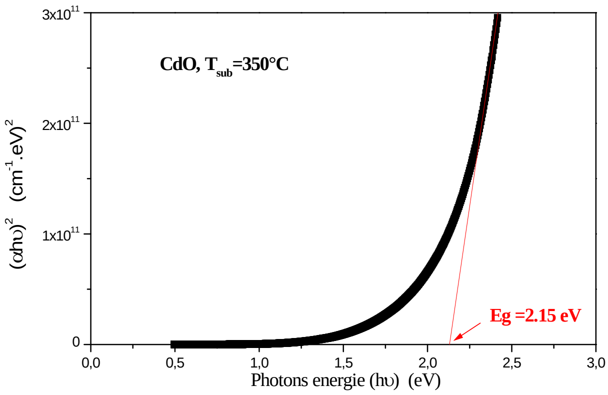


Fig.5. Variation of $(\alpha h\upsilon)^2$ versus (hυ) for CdO film deposited at 350°c.

2.4. Impedance analysis

Complex impedance diagrams (Z'' versus Z') of CdO with selected temperatures of 20°c, 40°c, 60°c, 80°c and 100°c are displayed on Fig. 6. The impedance diagrams are vertical lines for all temperatures. An equivalent electric circuit for our sample can be represented by a resistor R connected with a capacitance C in series, where R and C represents the grain resistance and capacitance of sample. The contribution of the grain boundary is masked; this is doing when the mean free path of free carriers is less than the size of the grain in the films [21] [22]. The real component and imaginary component values for such an equivalent electrical circuit are given by the following relations.

$$Z = R + \frac{1}{jC\omega} = Z' + Z'' \tag{3}$$

$$Z' = R \tag{4}$$

$$Z'' = \frac{1}{jC\omega} \tag{5}$$

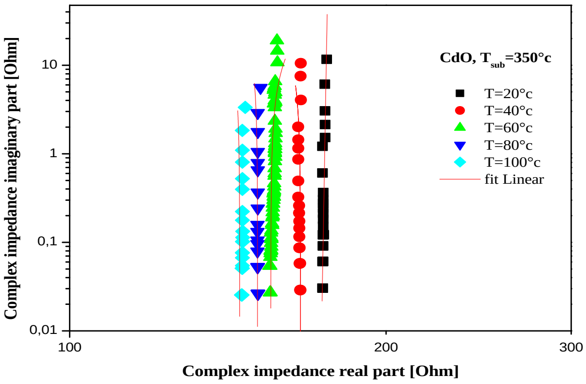


Fig.6. Niquist diagram of complex impedance (Z'' versus Z') of CdO

Fig. 7 and Fig. 8 shows respectively frequency dependence of real part Z' and the imaginary part Z'' of complex impedance Z at the different selected temperatures, in the semi logarithmic coordinates. Z' is independent of the frequency. The complex impedance real part (Z') in dependence with the temperature is represented by resistance R. The resistance decreases with the increasing temperature. Imaginary part (Z'') in dependence with the frequencies in the semi-logarithmic coordinates have an inclined line to each selected temperature, the value of Z'' correspond to capacity of the sample. It decreases with the increasing temperature too.

2.5. Electrical conductivity study

AC conductivity for the amorphous semiconductors increases with frequency according to universal power law of Jonscher described by following formula: [23]

$$\sigma_{AC}(\omega) = A.\omega^{S} \quad (6)$$

Where S is frequency exponent, A is a constant and ω is angular frequency. The AC conductivity values of the deposited CdO film were calculated at selected temperatures of 20°c to 100°c. Fig. 9 depicts AC conductivity versus frequency of as deposited film. From this figure, AC conductivity is independent of the frequency; no critical frequency of the change of the conductivity mechanism was seen. This result is indicative to the semi conductor materials behavior. The observation in this part of the study is that the CdO has a high conductivity strongly; thus allowing us to class him among the conductive oxides.

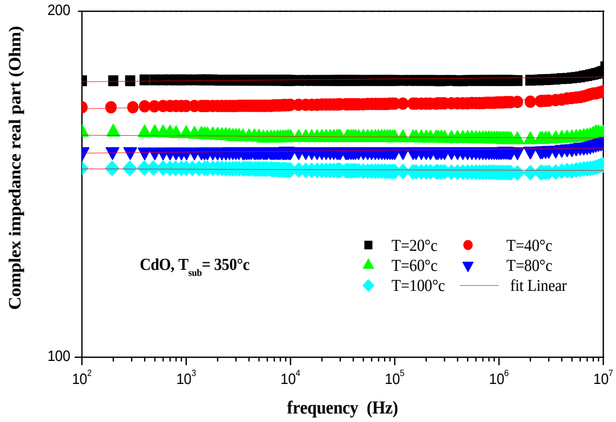


Fig.7. (Z’) versus Frequency and temperature

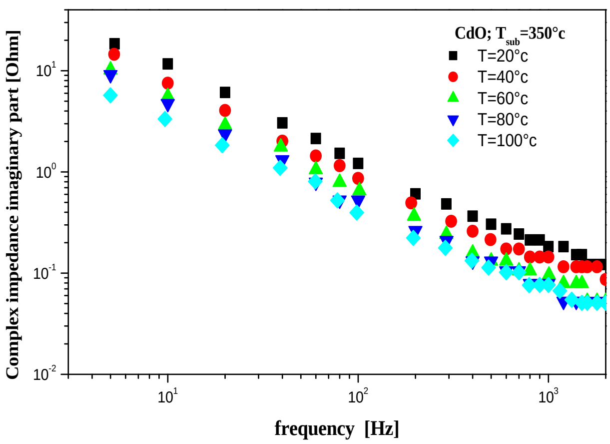


Fig.8. (Z’’) versus Frequency and temperature

The AC conduction behavior in materials is explained using different theoretical models [24]. In the consequence of the excitation, the transport of charges carriers between localized states, due to effect of the disorder in the films. Also, AC conductivity increases with the temperature. This rise of AC conductivity with the temperature is attributed to the process of thermal activation.

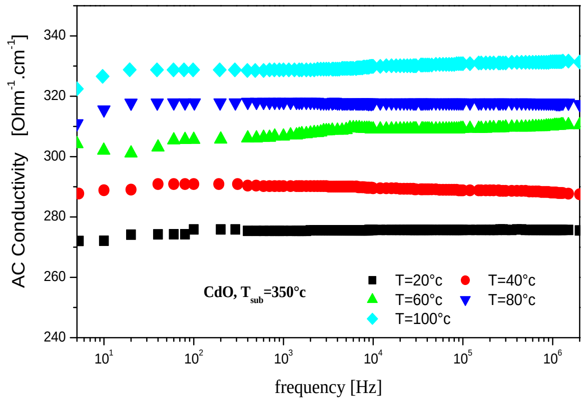


Fig.9. AC conductivity versus frequency and temperatures.

2.6. Dielectric properties study

Dielectric constant ε'and the dielectric losses ε" are calculated using following formulas [25]:

$$\varepsilon^* = \frac{\sigma^*}{i.\omega.\varepsilon_0} = \frac{\sigma''}{\omega.\varepsilon_0} - i.\frac{\sigma'}{\omega.\varepsilon_0} = \varepsilon' + i.\varepsilon'' \quad (7)$$

Where σ* is the total conductivity, ε_0 is permittivity of free space, and ω is angular frequency. Fig. 10 represents dielectric constant ε'(f) dependency of temperature and the frequency for investigated films of CdO. On the Fig. 10, the large values of dielectric constant towards the range of low frequency are attributed to the decrease in orientation polarization, which requires more time than other type of polarization and the dipoles may be not able to align themselves, so that their oscillations lag behind those of the field. Then, when applied field frequency is increased, the value of ε' decreases until it reaches a constant value. This phenomenon can be explained by the fact that the dipole will be completely unable to follow the field and the orientation polarization becomes negligible, the space charge polarization coming only dominant and related to dielectric constant. On other hand, increase of ε' with temperature is due to quantity of thermal excitation energy to be able to respond more easily to change in the external field. This in turn enhances their contribution to polarization leading to an increase of ε'. [21]

Dielectric loss (ε'') of the materials is represented by the imaginary part of their permittivity. The dependence of the dielectric loss ε"(f) on the frequency at the different temperatures is illustrated on Fig. 11; It decreases by increases in frequency at one constant temperature and increases by increases in temperature at constant frequency. Dielectric constant consists of two contributions: one of the low frequency DC conduction and the second one of the high frequency dielectric polarization process. At low and moderate frequencies, as the temperature increases, the conductivity increases, leading to a high dielectric loss value. This is in agreement with formula (8).

$$\varepsilon'' = \frac{\sigma'}{\omega . \varepsilon_0} \tag{8}$$

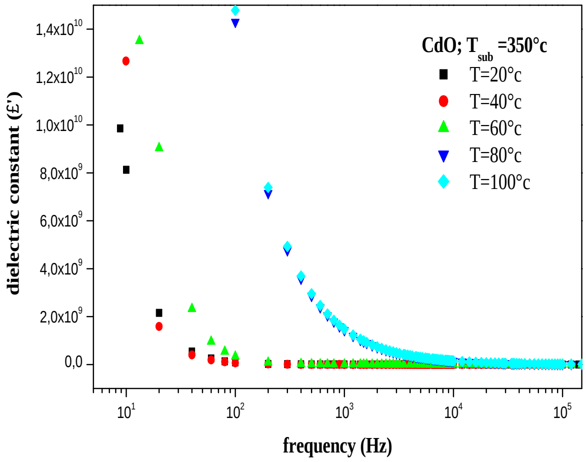


Fig.10. The variation of the (ε') with frequency and temperature for CdO film deposited at T_{sub}=350°

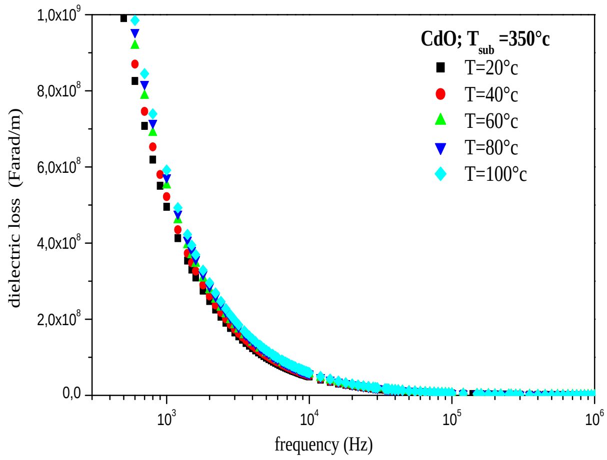


Fig.11. The variation of the (ε'') with frequency and temperature for CdO film deposited at T_{sub}=350°

3. EXPERIMENTAL

CdO in thin films were deposited by spray pyrolysis technique on glass substrate, which were cleaned before the vaporization chemical solution. They were immersed in acetone acid during 5min at least and washed in the ionized water then in the methanol alcohol and washed in the ionized water still a second liver, finally they were dried. The spray solution was about of the 0.1M concentration obtained by cadmium nitrate tetra hydrate $Cd(NO_3)_2.4H_2O$ dissolved in distilled water. The prepared solution was immediately sprayed to avoid any possible change in the solution with time. The end of capillary tube-substrate distance was maintained at 30cm, the substrate temperature of T_{sub}=350°C was controlled using a Chrome Nickel thermocouple. The pressure of air was of 7 bars. The spraying time was 20min. The thickness of these films calculated in order of 130nm using weighed method.

The X ray diffraction patterns of deposited films were recorded using Bruker's diffractometer (D8 Advance type) using Cu-Kα (λ= 1.5406A°) radiation in the 2θ range of 5-88°. The morphological and microanalysis of our sample were obtained on the microscopic electronic beam with a thermo electronic emission of the mark of LEO 1450VP. LEO 1450VP MEB is of nominal solving of 0.5nm to 30kV and a detector of Everhart- Thornley to detect the secondary electronics, and Si (Li) detector with a power selection for microanalysis of X qualitative and semi qualitative. The optical transmittance and reflectance were carried out in the wavelength range of (200-2500nm) using a UV-Visible JASCO mark V-570 double beam spectrophotometer. Electrical and dielectric properties were measured using the impedance spectroscopy technique [16], so the sample with a coplanar configuration was connected to the equipment of measurement which composed by a Hewlett Packard HP4192 analyzer and a thermocouple to regulate the temperature.

4. CONCLUSION

In this work, we fabricated and characterized the cadmium oxide in thin films. We used spray pyrolysis technique to produce thin films of CdO. It is economical technique, simple and capable to deposit a uniform and homogeneous layer. We brought out their properties. X-ray diffraction was used for structural analysis of the as deposited films. X-ray diffraction pattern was attributed to the CdO with polycrystalline structure of cubic phase, it showed that the crystallites of CdO films have a lattice parameter of 4.67Å, and nano-cristallite size of order of 35,158 nm. Random orientation ($P_{(200)}\approx 1$) was evaluated at very slow intensity of (200) peak. Morphological study shows that the grains of CdO films uniformly distributed on film surface, it was grown perpendicularly to the glass substrate, it appear under cylindrical shape. From optical study, optical gap of the Cadmium Oxide films was found equal to 2.15eV. The semi-conducting behavior of CdO in thin film was suggested from the impedance spectroscopy analysis. The CdO film has a high electrical conductivity and optical transmittance in the visible region of solar spectrum. Dielectric measurements revealed that both orientation polarization and space charge polarization were responsible for the enhancement of dielectric properties of CdO films.

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