Available online at www.elixirpublishers.com (Elixir International Journal)

Condensed Matter Physics

Elixir Condensed Matter Phys. 90 (2016) 37534-37536

ISSN: 2229-712X

Influence of Viscosity of Sol-Gel on the Properties of Cdo Thin Films by Spin Coating Method

P.Umadevi[1], M.Vivekanand[1] and N.Prithivikumaran[2]

[1]Department of Physics, Sri Vidya College of Engineering & Technology, Virudhunagar-626 005, Tamilnadu, India.

[2]Nanoscience Research Lab, Department of Physics, VHNSN College, Virudhunagar-626 001, Tamilnadu,India.

ARTICLE INFO

Article history:

Received: 17 November 2015;

Received in revised form:

2 January 2016;

Accepted: 7 January 2016;

Keywords

Cadmium Oxide,

Viscosity of Sol-Gel,

Structural Properties,

Electrical Properties,

Optical Properties.

ABSTRACT

Nanocrystallites of Cadmium oxide (CdO) thin films with different gelation time were deposited by sol-gel spin coating method on a glass substrate. A comparative analysis of the effect of viscosity of sol-gel on the structural, electrical, and optical properties of as deposited films was made. Films were grown with gelation time of one to four days and optimum gelation time of third day of sol-gel viscosity of 3.28 x 10^{-3} Nsm^{-2} was determined. From the X-ray diffraction studies the polycrystalline nature of the grown film with a preferential orientation (1 1 1) was analyzed. The resistivity of the material decreases with the increase of gelation time and then increases after the optimum value of gelation time. The films showed resistivity of 2.16 x 10^{-4} Ω m with an optical transmission of 80 % at the wavelength of 625 nm. The observed band gap of the developed film was found to be 2.25 eV. Also optical studies confirm that the optical transmittance was decreased when the viscosity was increased.

Introduction

Thin films of transparent conducting oxides (TCO) have been extensively studied because of their wide applications in the field of the electronic and photovoltaic devices. Among different TCO materials, Cadmium oxide is considered as a promising material for photovoltaic applications due to its high electrical conductivity and optical transmittance in the visible region of solar spectrum [1].Due to its low resistivity and high carrier concentration CdO is used in optoelectronic devices [2]. CdO is also an n- type semiconductor with rock salt crystal structure (fcc) and posses a band gap of approximately 2.5 eV [3]. Synthesis of CdO thin films have been reported by various researchers using different techniques such as sol-gel [4], Spray pyrolysis [5], DC magnetron sputtering [6], Chemical bath deposition [7] etc., Of these methods, sol-gel spin coating method is advantageous because of its simple and low cost of apparatus and highly reproducible results. Hence this technique is used in the present work.

In the sol-gel spin coating technique the viscosity of sol-gel plays a vital role to be considered, as it influences the film growth and the quality of the film. Highly conducting and transparent CdO thin films can be achieved by adjusting the viscosity of sol in to a proper value. CdO films have been already reported by Abdolahzadeh ziabari et al., [8] with gelation time of 24 hours and also D.M.Carballeda – Galicia et al, [9] with gelation time of 76 hours. By comparing with their results, the better crystallinity and the less value of band gap is obtained in this work. The study on the change in Physical properties of films in accordance with viscosity of sol-gel is very limited. In the present work, the influence of the viscosity of the sol-gel over the structural, electrical, and optical properties of the CdO films has been studied. For this purpose four CdO films were synthesized from one day to four days by sol-gel spin coating method and viscosity of sol-gel is investigated on every day of gelation time.

Experimental details

Thin Film deposition

The precursor solution for preparing the CdO films was obtained by dissolving cadmium acetate of 0.25 M (4.997 gm) in 75 ml of ethanol and adding 1ml of lactic acid to it to obtain the clear solution. The solution was constantly stirred using a magnetic stirrer for 2 hours at 65 °C. The obtained solution was kept in a beaker for aging. The sol-gel was used at every one day of interval for coatings till the formation of thick gel. The viscosity of the sol-gel was measured at every one day of interval by using Oswald's viscometer. The films were coated onto glass substrates (25 mm x 25 mm x 1.35 mm thickness). Prior to coating, the glass substrates were well cleaned with soap solution, chromic acid (at 60 °C for 2 hours) and washed with distilled water in ultrasonic bath for 20 minutes. The coating has been carried out using a microcontroller based spin coating unit. Eight successive coatings were made on the same glass substrate with a spin rate of 3000 rpm and a spin time of 15 s for each coating. After every coating the film was dried at 100 °C for 5 minutes to evaporate the excess solvent and to remove the organic residuals. After the final coating, the film was annealed in the muffle furnace at 400 °C for 1 hour. Finally nano crystalline CdO film was obtained on the glass substrate for first day. Similarly the nano crystalline CdO films was obtained for second, third and fourth day. As after fourth day the sol-gel gets saturated, the films are not deposited after gelation time of four days.

Characterization

The grown CdO thin film was confirmed by Powder X-ray diffraction technique using X – ray diffractometer (PA analytical – PW 340/60 X'pert PRO). The thickness of the prepared films was measured by Stylus profilometer SURFEST SJ – 301.The electrical characterization of the films

Tele:

E-mail addresses: janavi_p@yahoo.com

were made using Four probe methods. Optical transmission of CdO films were recorded in the range (300 nm-1100 nm) using Schimadzu UV-Vis-NIR spectrophotometer.

Results and discussion

Viscosity and thickness

The variation of viscosity and film thickness along with gelation time is shown in Figure 1. From the Figure, it is observed that both the viscosity and film thickness increases with gelation time. The film prepared with first day of gelation time was very thin and the transparency was also high. When the gelation time is increased, the film becomes fairly uniform and the film thickness increases slightly on second day. On the completion of third day, a uniform film coating with optimized film thickness was observed. A non uniform film coating with increased film thickness was obtained on the end of fourth day. Also it is confirmed that the gel becomes very thick after the completion of four days. Hence, the optimized value of viscosity and film thickness was found to be 3.28 x 10^{-3} Nsm^{-2} and 1.19 μm respectively.

Structural studies

X-ray diffraction patterns of the CdO films coated for various gelation times are shown in Figure 2. From the Figure 2, it is confirmed that all the CdO thin films were belongs to polycrystalline structure. The crystalline property increases when the gelation time was increased. The diffraction peaks of the films were indexed to (111), (200), (220), (311) & (222) and compared with standard bulk CdO pattern. The lattice parameter `a' for all the films found to be 4.63 Å which is in good agreement with the standard JCPDS data [JCPDS data card No. 75-0594].

The preferred orientation of the film was obtained by calculating the texture coefficient TC (h k l) for all the planes using the expression [10],

$$TC\,(h\,k\,l) = \frac{I(h\,k\,l)/I_0(h\,k\,l)}{\frac{1}{N}\sum_N I(h\,k\,l)/I_0(h\,k\,l)}$$

where TC (h k l) is the texture coefficient of the (h k l) plane, I the measured intensity, I_0 the standard intensity of the corresponding powder and N the reflections observed in the X-ray diffraction patterns. The TC values obtained for different planes for the various gelation times are shown in Figure 3.

From the Figure 3, it is observed that the TC value for (111) plane is the maximum for all the films which confirm that the (1 1 1) plane may be the most preferential orientation for all the films which was also reported by Jeyaprakash et al [11].

Various parameters such as crystallite size, micro strain, dislocation density and number of crystallites were calculated and Tabulated in Table 1.

The crystallite size of the films was calculated by using the Debye-Scherrer formula,

$$D = K\lambda/\beta\cos\theta$$

where k is constant, β is full width at half maximum of the peak and θ is the diffraction angle. The crystallite size value increases from first day to third day and decreases on fourth day. Micro strain in the film restricts the growth of grains [12]. From the table 2, it can be observed that the micro strain decreases from first day to third day of gelation time and then the strain gets increased on fourth day which decreases the crystallite size. Because of increase in crystallite size the voids were expelled and the films become denser, resulting in the increase in intensity of the observed diffraction peaks [13]. Crystalline nature also increases as the gelation time increases up to third day and then fall. This is clear from the peak intensity which is shown in Figure 2.The decrease in peak intensity after third day gelation time may be due to some sort of atomic disorder in the crystal lattice [14].The results indicate that third day gelation time of viscosity 3.28 x10^{-3} Nsm^{-2} is the optimum for preparing CdO thin films by sol-gel spin coating technique.

The micro strain in the films arises due to non uniform compressive (or) tensile strain developed in the film. The micro strain was calculated using the relation [15],

$$\varepsilon = \beta\cos\theta/4$$

The value of dislocation density (Δ) was calculated using the formula [16],

$$\Delta = n/D^2$$

Also using crystallite size 'D' and film thickness 't', number of crystallites per unit area (N) of the films was estimated using the relation [17],

$$N = \frac{t}{D^3}\ /\ \text{unit area}$$

It was observed that for the film with three days of gelation time and sol-gel viscosity of 3.28x10^{-3} Nsm^{-2}, the micro strain and dislocation density is lower than other films. It indicates that film with gelation time of three days and sol-gel viscosity of 3.28 x 10^{-3} Nsm^{-2} has a higher degree of crystallization.

Electrical studies

One of the reasons for the application of the CdO thin films in the optoelectronic devices technology is the good electrical conducting property. The variation of resistivity and crystallite size with gelation time is shown in the Figure 4. From the Figure it is observed that the gelation time increases the resistivity falls and reaches minimum value at third day of gelation time and then increases for further increase of gelation time.

As gelation time increases, the sol-gel becomes thicker and the crystallite size increases which may tend to reduce the grain boundary and increase the mean free path. The increase of mean free path may reduce the resistivity or improve the electrical conductivity of the CdO thin film. After third day of gelation time it can be seen that the resistivity increases.

Decrease in crystallite size on fourth day gelation time may increase the number of scattering centers and thus the electrical resistivity increases (i.e., conductivity decreases) [18]. Thus third day gelation time may be taken as optimum for preparing sol-gel spin coated CdO films for optoelectronic device fabrication. The resistivity value is obtained for the optimum condition is 2.16 x 10^{-4} Ωm which is having good agreement with the CdO films deposited by solution growth method [19]. The electrical conductivity of CdO thin film may be improved by adding various alkali metal ions.

Optical studies

The transmittance spectra of CdO thin films observed for different gelation time were shown in Figure 5. All the films show good optical transmittance of 75 % - 90 % above 600 nm wavelength. It was observed that the optical transparency of the films decreases with increase in gelation time (or) increase in film thickness. With increase in gelation time, the film thickness increases. As the thickness increases the surface roughness and density of localized state increases which reduces the transmittance value [20]. The transmittance decreases with increase in gelation time may be due to the considerable increase in film thickness and to the extra absorption of light that occurs at the grain boundaries of polycrystalline films [15]. The experimental results of Mahaboob Beevi et al [21] also indicate that the films of low thickness have high transmittance.

The band gap value E_g for the various gelation times was determined by using Tauc's relation,

$\alpha h\upsilon = A(h\upsilon - E_g)^n$

where α is the absorption coefficient ,hυ is the photon energy, E_g is the band gap and n=1/2 for the direct transitions. The direct band gap values for different gelation time were found to be varying from 2.6 eV to 2.1 eV which is shown in the Figure 6.It is observed that the direct band gap decreases with increasing gelation time or increase in film thickness.

In general, the density of localized state in the film increases with the film thickness which leads to decrease in the band gap. Such a variation in band gap with the increase of thickness has been reported by S.Sonmezoglu et al [22]. The decrease in the band gap with the increase in film thickness indicates that there is no charge accumulation at grain boundaries [23].

The transmittance of 80 % was obtained at 625 nm for the optimized gelation time. The band gap for the optimized gelation time was found to be 2.25 eV which is close to the reported value of 2.2 eV [24].

Conclusion

CdO thin films were successfully deposited by spin coating method with different gelation time. The films exhibit a preferential orientation along the (111) diffraction plane and belongs to a polycrystalline nature. The optimum value of viscosity was found to be 3.28 x 10^{-3} Nsm^{-2} from third day gelated film. Nearly 80 % of optical transmittance was observed and the band gap values vary from 2.6 eV to 2.1 eV for various gelation time. For an optimum gelation time the electrical resistivity was calculated as 2.16 x 10^{-4} Ωm.

References

1. Y.Yang, L.Wang, H.Yan, S.Jin, T.J.Marks, and S.Li, Applied Physics Letters, "Highly transparent and conductive double – layer oxide thin films as anodes for organic light-emitting diodes," 2006,89, 051116 - 051118

2. B.G.Lewis,D.C.Paine, MRS Bull. "Applications and processing of transparent conducting oxides," 2000, 25, 22 – 7.

3. J.Santos-Cruz,G.Torres-Delgado,R.Castanedo – Perez,S.Jimenez-Sandoval,J.Marquez – Marin,O.Zelya – Angel. Sol.Energy, "Influence of the growth parameters of p-CdTe thin films on the performance of Au-Cu /p-CdTe /n-CdO type solar cells", 2006, 80, 142 - 147.

4. D.M.Carballeda-galicia, R.Castanedo–Perez, O.Jimenez-Sandoval, S.Jimenez-Sandoval, G.Torres-Delado, C.I.Zuniga – Romero, Thin Solid films, "High transmittance CdO thin films obtained by the sol-gel method", 2000,371, 105 -108.

5. C.H.Bhosale,A.V.Kambale,A.V.Kokate,K.Y.Rajpure, Materials Science and Engineering B, " Structural ,optical and electrical properties of chemically sprayed CdO thin films", 2005, 122, 67- 71.

6. Q.Zhou, Z.Ji, B.Hu, C.Chen, L.Zhao, C.Wang, Mater.Lett., " Low resistivity transparent conducting CdO thin films deposited by DC reactive magnetron sputtering at room temperature", 2007, 61, 531 - 534.

7. S.Dhawale, A.M.More, S.Latthe, K .Y. Rajpure, C. D. Lokhande, App.Sur.Sci., "Room temperature synthesis and characterization of CdO nanowires by chemical bath deposition (CBD) method", 2008, 254, 3269 – 3273.

8. A.Abdolahzadeh Ziabari and F.E.Ghodsi, Acta Physica Polonica A, Acta Physica Polonica A "Optical and structural studies of sol-gel deposited Nanostructured CdO thin films:Annealing effect", 2011,120, 536 – 540.

9. Z.Serbetci, B.Gunduz, A.A.Al-Ghamdi, F.Al-Hazmic, K.Arik,F.El-Tantawy, F.Yakuphanoglu and W.A.Farooq, Acta Physica Polonica A, "Determination of optical constants of nanocluster CdO Thin films deposited by sol- gel technique", 2014,126, 798 – 808.

10. C.Barret,T.B.Massalski,Structure of Metals,Pergamon Press oxford,1980.

11. Jeyaprakash B.G, Bull.Mater.Sci, "Temperature dependent grain size and microstrain of CdO thin films prepared by spray pyrolysis method", 2011, 34,601- 605.

12. Mustafa ¨Ozta, Chin Phys. Lett., "Influence of Grain size on Electrical and Optical properties of InP films", 2008, 25, 4090 – 4092.

13. W.Buckel,Structure and properties of Thin Films,Wiley,Newyork,1 959,P-53

14. E.Savarimuthu, N.Sankarasubramanian, B.Subramanian, M.Jayachandran, C.Sanjeeviraja and S.Ramamurthy, Surf.Eng, "Preparation and characterization of nanostructured tin oxide (SnO_2) films by sol – gel spin coating technique", 2006,224, 268- 276.

15. P.P.Sahay, R.K.Nath, &S.Tewari, Cryst.Res.Technol., "Optical properties of thermally evaporated CdS thin films", 2007,42, 275 - 280.

16. R.L.Mishra,A.K.Sharma,&S.G.prakash, Digest.J.Nanomater.Bio struct. "Gas sensitivity and characterization of cadmium oxide (CdO) semiconducting thin film deposited by spray pyrolysis technique", 2009, 4,511 - 518.

17. A.R.Balu,V.S.Nagarethinam,M.Suganya,N.Arunkumar,G. Selvan, Journal of Electron Devices "Effect of the solution concentration on the structural,optical and electrical properties of SILAR deposited CdO thin films", 2012,12, 739-749.

18. R.Rajammal,K.Rajaram,E.Savarimuthu and S.Arumugam, Surf.Eng.,"Influence of number of coatings on properties of sol-gel spin coated CdO thin films", 2012,28, 205-208.

19. A.J.Varkey,A.F.Fort, Thin Solid Films, "Transparent conducting cadmium oxide thin films prepared by a solution growth technique", 1994, 239, 211-213.

20. N.Kumar,U.Parihar, R.Kumar, K.J.Patel,C.J.Panchal, N.Padha, American Journal of Materials Science, "Effect of film thickness on Optical Properties of Tin Selenide Thin Films Prepared by Thermal Evaporation for Photovoltaic Applications", 2012, 2,41-45.

21. Mahaboob Beevi, M.Anusuya & V.Saravanan, Int.J.Chem.Eng.Appl. "Characterization of CdO thin films prepared by SILAR deposition technique", 2010, 1, 151-154.

22. S.Sonmezoglu, A.Arslan, T.Serin and N.Serin, Phys.Scr. "The effect of film thickness on the optical properties of film thickness on the optical properties of TiO_2 – SnO_2 compound thin films", 2011, 84,065602 - 065607.

23. M.Pandiaraman,N.Soundararajan,C.Vijayn, Journal of ovonic Research, "Effect of Thickness on the optical bandgap of silver-Telluride Thin film", 2011, 1,21 - 26.

24. J.Santos-Cruz, G.Torres-Delgado, R.Castanedo-Perez, S.Jimenez-Sandoval, C.I.Zuniga-Romero, J.Marquez-Marin and O.Zeleya-Angel, Thin solid films "Dependence of electrical and optical properties of sol-gel prepared and doped cadmium oxide thin films on annealing temperature", 2005,493, 83-87.