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Study of Structural and Mechanical properties of Zirconium Doped Cadmium Sulphide Thin Films

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Abstract:

Thin films of Zirconium doped Cadmium Sulphide are grown from aqueous solution at temperature of 250^0C by spray pyrolysis technique. The films were characterized by X-ray diffraction (XRD). It reveals that the films are of polycrystalline nature with grain size in the order of nanometers. Depth sensing indentation is a powerful experimental tool for determining mechanical properties of thin film. Present work is based on Oliver-Pharr theory to measure hardness and elastic modulus by using ultra low load micro hardness indenter unit. SEM studies indicate that the grains are uniformly distributed throughout the sample area.[Journal of American Science 2009:5(3) 26-30] (ISSN: 1545-1003)

Keyword: Thin films; Elastic modulus; Hardness; Indentation testing

1. Introduction

The term 'thin film' generally refers to layer of material with one dimension much smaller than the other two. Thin film materials have become technologically important in recent years. Some examples are Microelectronic integrated circuits, Magnetic information storage systems, optical, wear resistant and corrosion resistant coatings. The use of materials in thin film form is the need for small-scale devices, physical properties that are scale-dependent and cost benefits. Although many of thin films based devices are limited by their mechanical properties and hence it is important to understand it. Thin films of doped CdS have been prepared by many techniques such as chemical bath deposition [Kodigala Subba Ramaiah et al., 2001] thermal evaporation [A. Ashour, et al., 1995] etc., Out of many methods available Spray Pyrolysis technique found to be simple and cost effective and has some advantages over other methods. This method is quite simple and flexible for process modifications. Additionally, by using this technique one can produce large area films without the need of an ultra high vacuum and the produced films can be controlled step by step.

Mechanical properties of thin films have been an interesting research topics and an indentation technique has been developed for studying them [W.C.Oliver and G.M. Pharr 1992, J.Mencik and M.V. Swain, 1994]. Although many researchers have investigated mechanical properties of different kinds of thin films on various substrates [M.Wittling, et al., 1995, T.Y. Tsui, et al., 1999, T.Y.Tsui, et al., 1999]. In this work, Zirconium doped Cadmium Sulphide film prepared by Spray Pyrolysis method on glass substrate has multiple tribological applications, such as favorable oxidation, corrosion resistance and enhanced wear resistance [V. Portinha, et al., 2003]. The tribological properties of the coated substrate system usually connected to hardness, elastic modulus and adhesion. These physical quantities are usually influenced by the chemical composition, micro structure, and substrate morphology which are dependent on the deposition condition and preparation methods.

The most common method to measure hardness is indentation type. The indentation-hardness is found to depend on the film micro structure [S. Miyabe and Aono N.Kitazawa, 2002]. In this, a diamond indenter is pressed on the surface of the specimen and after removal; it leaves an impression according to the indenter used. The hardness is estimated from the ratio of the load applied on indenter to the area of the impression left on the specimen. Note that this technique provides a possibility to evaluate mechanical properties in 'real' values, i.e. the influence of substrate material is eliminated since the maximum deep of indentations remains lower than 10-15% of the coating thickness [J.V.Fernandes, et. al., 2000,]. Using a DUH 211/211-S Shimadzu Ultra low load micro hardness tester, elastic modulus and hardness were calculated from one of the Sneddon's solutions [I.Sneddon, 1965] leads to simple relation between the load (P) and penetration depth (h) of the form

$$E_r = \frac{\sqrt{\pi}}{2} \cdot \frac{S}{\sqrt{Ac}} \qquad \text{------------- (1)}$$

Where S=dP/dh known as contact stiffness. Elastic modulus can be taken directly from the initial unloading slope S, A is contact area. According to Hertz equation combined elastic modulus specimen/indenter (E_r) is,

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad \text{------------ (2)}$$

Where E, E_i, ν and νi are the elastic moduli and Poisson's ratio of the specimen and indenter respectively. For diamond which is the usual material of Vickers indenter, E_i = 1141GPa and ν_i = 0.07.

2. Experimental Methods

Zirconium doped Cadmium Sulphide thin film were prepared from the precursor solutions, containing salts of Cadmium Acetate ($Cd(CH_3COO)_2.2H_2O$ – 0.1M), thiourea (CH_4N_2S - 0.1M) and Zirconium Oxy Chloride ($ZrO_2Cl_2.8H_2O$ - 0.05M) in double distilled water along with the complexing agent Ethylene-Diamine-Tetra-Acetic acid (EDTA) ($C_{10}H_{16}N_2O_8$) of 0.1M is chooses to stabilize the grain size. The Spray Pyrolysis setup consists of a substrate heater, spray gun, air compressor, solution reservoir and a gas exhaust unit. Details of this setup have been published elsewhere [A.Ashour, 2003]. The air pressure is kept around 1.1 bars, the solution flow rate is fixed to 0.2 ml per minute and the spraying time ranged between 1-2 seconds. The aqueous solution was then sprayed on the preheated glass substrate kept at 250^0C. Films of different thicknesses were prepared by varying the amount of solution sprayed and keeping all other parameter same. The terminal thickness of the film was measured by gravimetric technique and it is found to be in the order of 650 - 700 nm.

3. Result and discussion

3.1 XRD Analysis

XRD pattern of the Zirconium doped Cadmium Sulphide films were studied at room temperature by using RIGAKU diffractometer (model RAD II A) with CuKα radiation (1.5418 Å) where other radiations are suppressed using Ni filter. The data were recorded at a scan rate of 0.2^0/min and in the range of $20^0 < 2\theta < 80^0$. The crystallinity pattern of as deposited film on clean glass substrate prepared by Spray Pyrolysis technique at 250^0C is shown in Fig. (1). Observation of the film shows smooth surface and well adhesive nature of the film with substrate. The peaks observed in all the diffractograms confirm the nanocrystalline nature of the Zirconium doped Cadmium Sulphide thin film. The pattern also reveals the film is polycrystalline with cubic crystal structure and preferential orientation along (111) plane.

The other strong peaks observed correspond to the (200) and (222) orientations. Also the intense peak oriented along (111) lattice plane indicates that the growth of the grains is parallel to the substrate. The diffraction peaks appears in the spectrum have been identified as 26.94º, 31.14^0 and 55.07^0 which is verified with the known patterns of standard X-Ray Diffraction data file (JCPDS file No: 80-0019) X-ray diffraction line broadening (XDLB) was used to estimate the grain size of the film by utilizing Scherrer's formula

Where k is the shape factor constant

$$D = \left[\frac{K\lambda}{\beta\cos\theta}\right] \quad \text{------(3)}$$

(0.89), λ is the wavelength of CuKα line, θ the Bragg's angle of reflection, β full width half maximum (FWHM) of intense peak. The mean grain size of as deposited film is calculated using Scherer's equation is 30nm. Here, the grain size calculated by Scherer's formula is less than 50 nm. This small grain size is due to the evaporation of individual fine droplets during the sprayed process and be due to EDTA effect with doping material of Zirconium. In this present work, the co-ordination bonds of doping element with complexing agent are not dealt rather focused on hardness for the observed grain size.

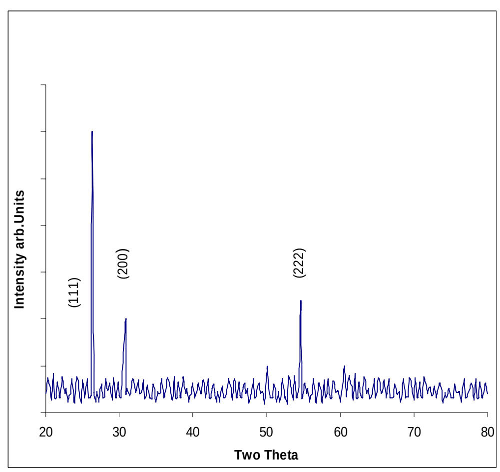

Fig. 1. XRD pattern of 0.05M of Zirconium doped Cadmium Sulphide thin film prepared at 250ºC

3.2 Mechanical Properties studies

Mechanical properties were studied by a instrumented indentation method using a DUH 211/211-S Shimadzu Ultra low load micro hardness depth sensing indentation machine equipped with a Vickers diamond pyramid indenter. Its tips radius is 0.1μm. Measurements of hardness and elastic modulus have been performed for different loads 1-7 mN by the following procedures of Oliver - Pharr theory. Measurements were made in this work by increasing the loading force in simple steps, to the maximum force of 7 mN, then decreasing the loading force by the same steps. Loading / unloading time was constant for all indentations which mean that loading rate was essentially different for different maximal loads. In Figure (2), local values of hardness (H) and elastic modulus (E) were calculated for every load Vs depth curve using equations (1), (2) and (4) respectively. The hardness measurements of the Zirconium doped Cadmium Sulphide with molarity of 0.05M prepared with the complexing agent (EDTA) of 0.1M deposited at 250°C were recorded as a function of loading force 1-7 mN are as shown in Fig.(3). It reveals that the hardness of the film slightly increases with increase in load of 1-7 mN. At loads greater than 7 mN, the hardness saturates to a constant value. Typically, the measured hardness has at 7 mN load. The maximum depth of the indent made by Vickers diamond probe tip is only 62nm, which is less than 1/10 of the Zirconium doped Cadmium Sulphide thin film thickness. The substrate effect is thus eliminated. The Poisson ratio of the as deposited coatings was estimated as ν =0.3. Due to the fact that it enters as $(1-\nu^2)$ in the calculation of E, an error in the estimation of the Poisson ratio does not produce a significant effect on the resulting value of the elastic modulus.

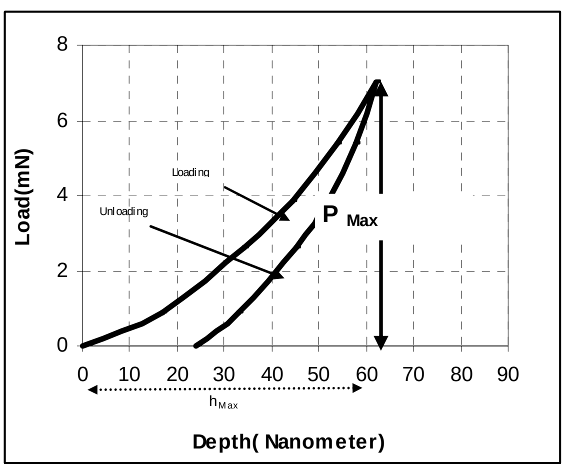

Fig. 2. Load Vs Depth curve of Zirconium doped Cadmium Sulphide thin film prepared at 250^0C

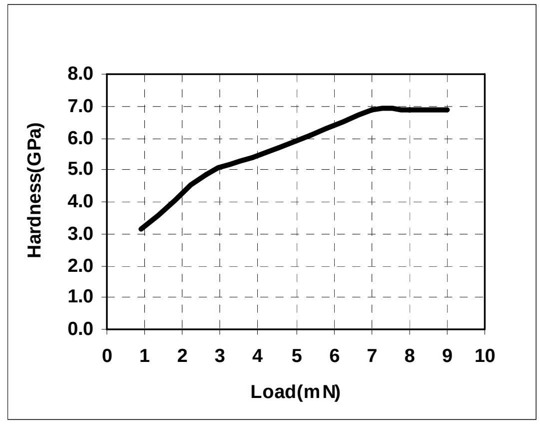

Fig.3. Load Vs Hardness of Zirconium doped Cadmium Sulphide thin film prepared at 250^0C

Using the set of experimental curves obtained for every type of coating, average values of H and E as a function of depth were generated, together with the corresponding standard deviations.

$$H_V = 1.854 \frac{p}{d^2} \quad \text{------------ (4)}$$

Where H_v is the Vickers hardness, it is expressed in GPa, P is the load applied on indenter in mN and d is the diagonal length of the impression in micrometer. In view of the scattering in hardness data, a number of indentations are made for each load and each value is taken from the average of five close measurements. The hardness H calculated from Equation (4) using the projected area. The calculated value of hardness is as deposited film at maximum load is 6.89GPa.

Fig.4. Elastic Modulus Vs Hardness of Zirconium doped Cadmium Sulphide thin film prepared at 250^0C

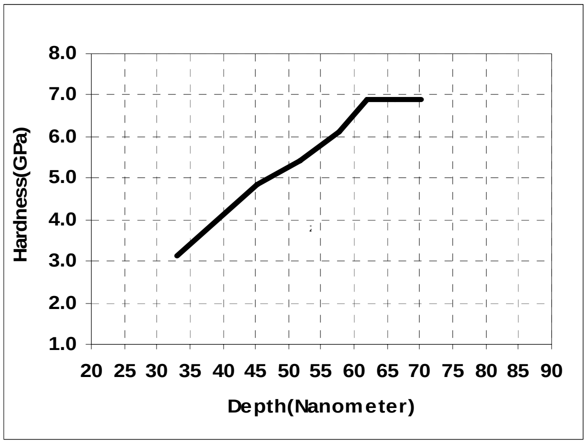

Fig.5. Hardness Vs Depth of Zirconium doped Cadmium Sulphide thin film prepared at 250^0 C

It is higher than the literature value of undoped Cadmium Sulphide bulk material [Marian Vrbanczyk, et. al., 2005]. It attributes doping material is stronger in nature. The value of contact stiffness S is calculated from the slope of unloading curve is as shown in Fig. (2). The calculated value of elastic modulus is as deposited film at maximum load is 56.12GPa. It is higher than the literature value of undoped Cadmium Sulphide bulk material [Marian Vrbanczyk, et. al., 2005]. Fig. (4) Shows that the correlation between hardness and elastic modulus. Clearly from this figure, there are no consistent and definite correlations for all the Sulphide materials. It infers that the value of elastic modulus calculated from Eq (1) and (2) of prepared films converges approximately to 56.12GPa and found to increase as hardness increases which lead to elastic nature. It turned out, however, that there exists a relatively good correlation between in these two properties for the parallel direction to the layer plane of pyrolytic Cadmium Sulphide thin films. In particular, elastic modulus values of Spray Pyrolytic Zirconium doped Cadmium Sulphide thin films were in the range of 46.4 GPa to 56.12GPa although the hardness values were largely different from each other. It seems that the reason why the elastic modulus is relatively high compared to the hardness value is that many fine pores may contribute to it. The average value of the hardness is calculated from the indentation data without considering the shallowest indentations is approximately 6.8GPa. Therefore one can conclude that the highest value of hardness at maximum load of the film is 6.89GPa and the elastic modulus is 56.12GPa. Hardness found to increase as load increases there by the film becomes stronger in nature.

Fig. (5) Shows for higher indentation depths the hardness increases significantly. It presents the result of hardness measurement obtained for the surface of the as deposited film. As can be seen, the dependence of the hardness on contact depth is highly pronounced. Starting with a value of 3.1GPa at indentation depth of 33nm, the hardness increases as the depth increases, reaching a plateau of approximately 6.89GPa. Accurate measurement of the displacement of the tip during indentation process allows us to calculate other mechanical properties from load and depth (P-h) curve. The values are calculated from initial portion of the slope of unloading curve as suggested by Oliver-Pharr theory. Hardness was also shown to be related with grain size and surface roughness. The hardness increases as increasing in depth upto a particular load, further the hardness increases and it attains a constant value. The hardness increases for lower grain size in lower load, this fact is in agreement with other studies and is attributed to the increase in the number of grain boundaries, which, in turn, increases the surface energy and reduces dislocations.

3.3 SEM Analysis

The SEM micrograph of the Zirconium doped Cadmium Sulphide thin film deposited *on a clean glass slide* at 250^0C is taken using cold field emission of SEM (JEOL, JSM 6701F, Japan) to support the XRD observations. *Prior to the observation*, using an auto sputter fine coater (JFC 1600, JEOL Japan) *about 50A⁰ gold was sputtered on the thin film surface for better contrast and to avoid charge accumulation*. Surface morphology of the film prepared at 250^oC is shown in the Fig. (6). It shows that grains are distributed with uneven shape and are not well connected to each other which reflect the hardnessand rough surface of the film.

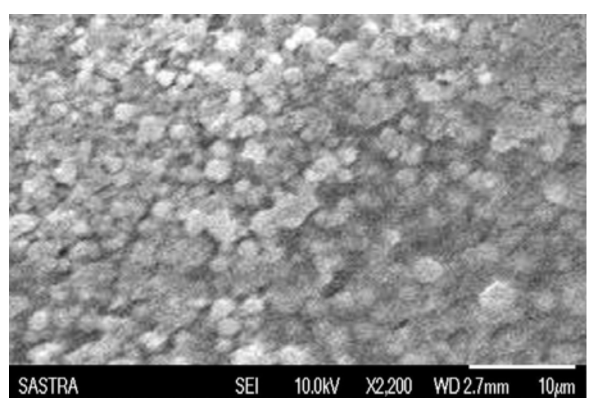

Fig. 6. SEM image of Zirconium doped Cadmium Sulphide thin film prepared at 250^0c

Conclusion

In view of the experimental results and discussions the following are the key observations. Thin films of Zirconium doped Cadmium Sulphide were grown on glass substrate at 250^0C by spray pyrolysis technique. XRD analysis confirms the formation of poly crystalline nature. Using Low load micro-hardness indentation tester; at maximum load the estimated elastic modulus and hardness values are 56.12GPa and 6.89GPa respectively. It is found that elastic modulus increases with increase in hardness. Morphology of the prepared film indicates the rough nature of the film. Further work has to be done to improve the morphology of the film. The established conditions for synthesis of Zirconium doped Cadmium Sulphide might have technological implications in the development of sensors, fuel cells, solar cells masks for nanotechnology and catalysis.

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