EFFECT OF ANNEALING ON CdS FILMS PREPARED BY ELECTRON BEAM EVAPORATION

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ABSTRACT

The structural properties of CdS films, prepared by electron beam evaporation technige (EBET) was studied by X-ray diffraction and transmission electron microscopy (TEM) using amorphous and crystalline substrates. The best degree of crystallinity was observed for films deposited on mica substrates. Initial stage of recrystallization of films deposited on mica substrates. Initial stage of recrystallization of films deposited on amorphous substrates has occured due to transfer of part of the energy of the TEM beam into heat in the film. CdS films, deposited on glass substrates, when annealed in vacuum at 520 K for 2 h, showed monocrystalline hexagonal structure.

INTRODUCTION

The evaporation of compounds is a complicated process, because usually the vapour pressures of the elements of the compound differ from each other. Consequently the composition of the evaporated material can differ in its stoichiometry from that of the original compound. EBET has been successfully applied for the preparation of refractory materails[1] and oxides[2,3] beside their excellent application for elemental substances.

Cadmium sulphide is one of the important materials, used for solar cell fabrication. Films are usually prepared by thermal evaporation, and other techniques[4-10].

In the present work we aimed to :

(a) Prepare thin CdS films by EBET technique and to study the structure of the films by electron diffraction (ED) and X-ray diffraction.

(b) Compare the structural features of the films prepared by TET and EBET using ED technique.

(c) Study, by ED technique, the structure of the films annealed by either the TEM electron beam or thermally annealed under vacuum.

EXPERIMENTAL

CdS films up to 2600nm thick were prepared by EBET under vacuum of 10^{-4} Pa with an electron beam of 0.2 kw power. For this purpose an Edwards 306 coating unit supplied with an electron beam attachment was applied. Glass, quartz slides, silicon single crystal wafers and mica sheets were applied as substrates for the deposited films. X-ray diffraction patterns of CdS films were obtained for the different substrates. Using the conventional thermal evaporation technique (TET), we prepared CdS films which were used only for comparison with films prepared by EBET technique. TEM and ED patterns of CdS for carbon - coated copper grids were obtained. Mica sheets as an example of crystalline substrates were used for TEM study. Films on amorphous substrates (glass) were annealed at 520K for 2 hr under vacuum of 10^{-4} Pa. The films were deposited on glass slides instead of carbon-coated copper grids for easy handling. Electron microscope (Siemens, Germany) working at high tension power supply up to 100 KV with magnification up to 100.000 X was used.

3 - RESULTS AND DISCUSSION

1 - Transmission Electon Microscopy and Electron Diffraction

Fig. 1 (a,b) shows a comparison between TEM micrographs of as - deposited CdS films prepared by TET Fig. 1 (a) and EBET Fig. 1 (b) (Film thickness = 220 nm on carbon - coated copper grids) The average values of the particle sizes for TET and EBET are close to each other (=40nm). At should be noticed that the magnifications of the two micrographs are different. CdS particles, obtined by

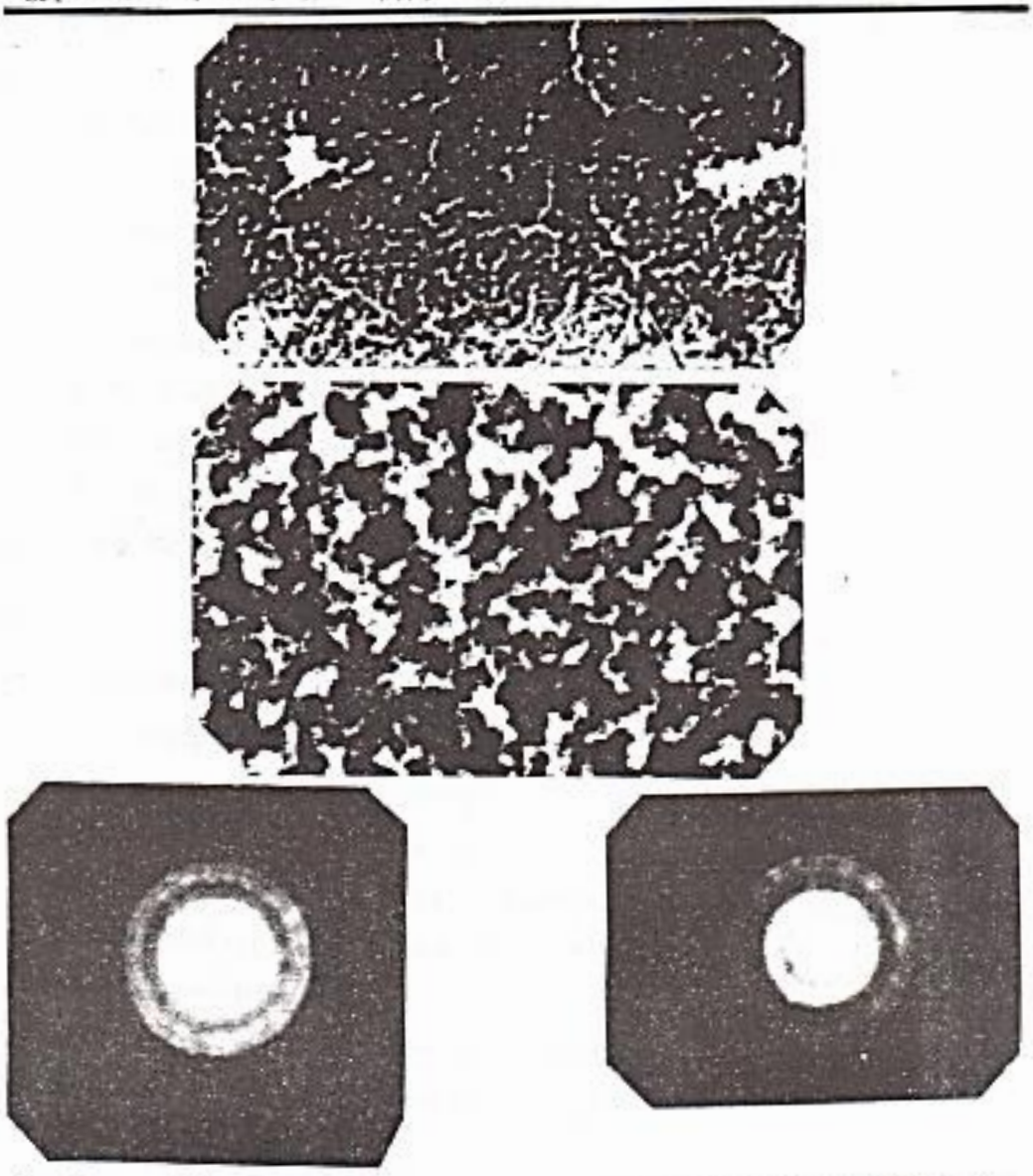

Fig. 1 : TEM micrograph of CdS film, deposited on carbon by TET, magnification is 40.000 (a), TEM micrograph of CdS film deposited by EBET, magnification is 70.000 X (b) and a representative ED pattern (c).

Fig. 2 : TEM of CdS film, deposited on carbon by EBET after electron beam annealing : micrograph with magnification 146100 X (a) and ED pattern (b).

TET Fig. 1 (a) and EBET Fig. 1 (b) show hexagonal morphology. The particles in Fig. 1 (a) are better arranged than those in Fig. 1 (b). It is well known that the structural features of the deposited films depend on the technique of evaporation. The difference between the films in Fig. 1 (a) (prepared by TET) and the film in Fig. 1 (b) (prepared by EBET) is most likely due to the fact that for EBET films, the source material was heated locally due to the focussed bombarding electron beam yielding a jet of vapours, which then condensed onto the cold substrate. However, for TET films the source material and the substrate were heated globally and homogeneously. This allowed for better growth and arrangement of the crystallites.

Fig. 1 (c) shows a representative ED pattern, for films prepared by either TET or EBET indicating a polycrystalline nature for both films. From the calculations of the obtained electron diffraction rings, the interplanar spacing (d-values) were compared with those taken from the X-ray ASTM cards. Referring to those ASTM cards, it was found that CdS films deposited by TET and EBET have hexagonal wurtzite structure of space group P63 mc and unit cell parameters a = 0.413nm, c = 0.6713 nm. The calculated unit cell parameters are a = 0.4157 nm and b = 0.6596 nm. After few minutes of exposure to the electron beam, of the electron microscope at 80 kv and 1.5 μA incident current, ED patterns gave scattered spots instead of continuous rings. This is suggested to be to recrystallization of the film as shown in Fig. 2 (b).

Generally the heat transferred to the film, leading to the temperature rise[11], depends upon the elctron beam parameters. This temperature rise can be responsible for the recrystallization. The effect of electron beam bombardment was observed previously by the cathodoluminescence results reported[12] for both scanning and stationary modes, where outdiffusion of defects and reevaporation of CdS occured.

A representative TEM micrograph of CdS films, deposited on mica substrate is shown in Fig. 3, which shows the growth of well arranged[10] hexagonal CdS crystallites with sharp edges and particle sizes in the range of 100 : 450 nm. The

Fig. 3 : TEM of CdS, deposited on mica substrate by EBET, magnification is 40,000X.

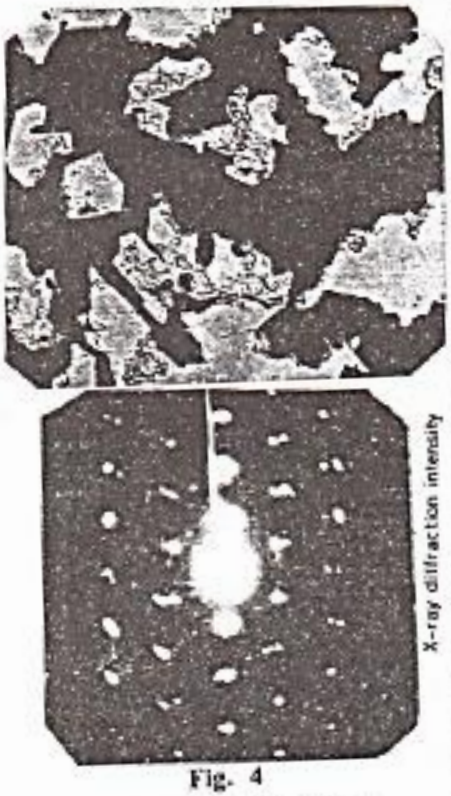

Fig. 4

TEM of CdS, deposited on glass substrate by EBET after thermal annealing vacuum at 520 K : micrograph with magnification 51690 X (a) and ED pattern (b).

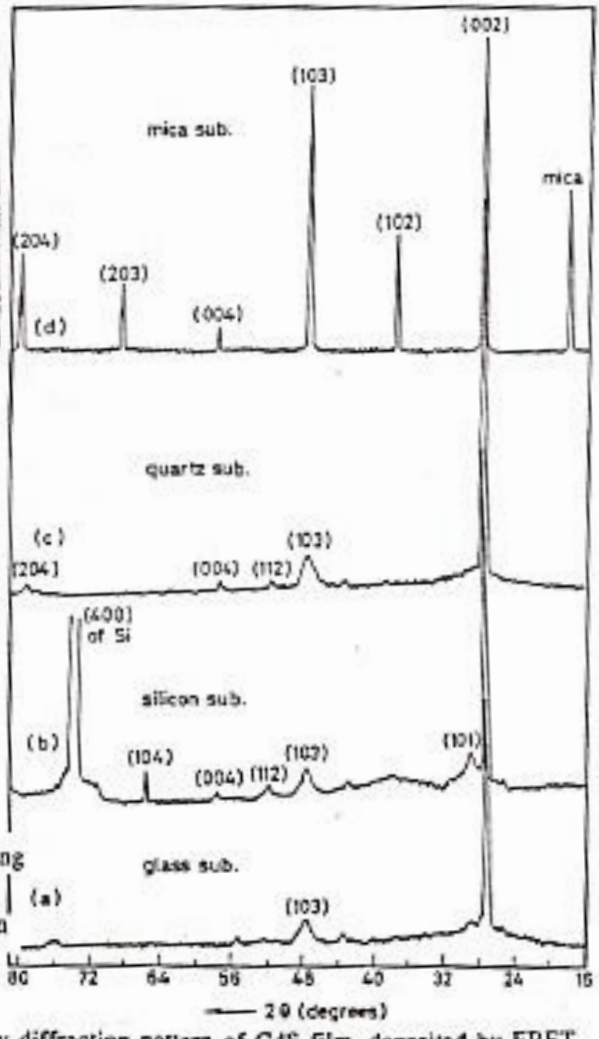

Fig. 5 X-ray diffraction pattern of CdS film, deposited by EBET on glass, silicon, quartz and mica substrates.

average particle size is 200 nm. This particle size is five times larger than that deposited on carbon - coated copper grids. The crystal growth on mica occurred in preferred sites of the cleavage plane of mica. Fig. 4 (b) shows a representative ED pattern of CdS films deposited on glass by EBET, then annealed under vacuum of 10^{-4} Pa at 520 K for 2h. Spot diffraction pattern idicates the monocrystalline structure of the annealed CdS films. From the analysis of such spots we obtained that they have the following interplanar spacings : 0.186 nm, 0.1698 nm and 0.096 nm. These values correspond to the ASTM values 0.1898 nm, 0.1791 nm and 0.0973 nm corresponding to (103), (200) and (304) planes of CdS respectively. This may be interpreted by twinning of some crystallites. Fig. 4 (a) shows the corresponding TEM micrographs of the film. Recrystallization and reevaporation took place, in some regions of the film as indicated by empty areas with nearly hexagonal edges. The reevaporated particles are suggested to have sizes in the range of 80:250 nm which are approximately equal to those of the unannealed films on mica substrates. This enables us to suggest, that in order to obtain crystalline films, the material is either deposited on crystalline substrates or on amorphous (glass) substrates, followed by thermal annealing under high vacuum at a suitable temperature. Comparing the electron diffraction patterns of CdS films Fig. 1 (c), 2(b) and 4(b) we observed the following :-

A - Fig. 1 (c) shows that the as-deposided film possesses polycrystalline structure as observed from the continuous rings of the electron diffraction.

B - Fig. 2 (b) shows that, after exposure of the film to the electron beam of the TEM, the first stage of recrystallization took place since scattered spots were observed.

C - Fig. 4 (b) shows that by thermal annealing of CdS films (deposited on glass substrates at 520K for 2 h under vacuum) well arranged spots are displayed showing the hexagonal structure of CdS films of (001) zone axis.

2 - X-ray Diffraction Results

Fig. (5) shows X-ray diffraction patterns of CdS films prepared by EBET on glass (curve a), silicon single crystal wafer (curve b), amorphous quartz

(curve c) and mica sheet (curve d) for film thickness of 1000 nm and evaporation rate of 0.75 nm/sec. Notice that for representation of Fig. (5), the relative intensity of CdS deposited on mica is reduced by 50 times its real value on the X-ray chart. The interplanar spacing, d-values, corresponding to each peak for all substrates, were calculated and compared with the standard d-values in the ASTM cards. The corresponding (hkl) reflections were identified as shown in Fig. (5). The experimental d-values agreed with those from ASTM cards. It appears that for glass, silicon and quartz substrates, polycrystalline films with (002) preferred orientation are obtained[7,10,13]. This means that for glass and quartz amorphous substrates, polycrystalline films are expected to occur. In the case of single-crystal substrate, the polycrystalline CdS film may occur due to a native existing amorphous thin silicon oxide layer upon silicon. The amorphous natural oxide layers upon silicon surfaces are grown usually at the ambient atmosphere. This may mask the silicon single crystal, leading to polycrystalline CdS film. For CdS film on mica substrates sharp high-intensity peaks are observed.

The X-ray results reveal the crystalline structure for amorphous and crystalline substrates which agree with the TEM results.

4 - CONCLUSIONS

From the present study we can conclude the follwoing :

1- As given from the ED results of the TEM, for TET and EBET the CdS films deposited on amorphous substrates (carbon or glass) have polycrystalline hexagonal structure.

2- Films, deposited on crystalline substrates (mica sheets) shows comparatively larger particle size than those of amorphous substrates.

3- Thermal annealing of polycrystalline CdS films deposited on amorphous substrates led to recrystallization of films.

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