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Recrystallization processes in screen-printed CdS films

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Abstract. Kinetics of recrystallization in screen-printed polycrystalline CdS films has been investigated by X-ray structure analysis and optical microscopy. The relation between the crystallite size, crystallite orientation and the macrostrain, as well as their dependence on heat treatment regimes is established. It is shown that single-phase CdS films having a thickness of some tens microns, large grain size and low residual strain can be produced at optimum technological regimes. The films obtained are suitable for fabrication of CdS/CdTe solar cells.

Keywords: CdS film, screen printing, structural perfection, recrystallization, solar cell

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1. Introduction

n-CdS/*p*-CdTe heterojunctions whose efficiency of solar energy conversion may be as high as 16% [3] are considered to be one of the most promising candidates for fabrication of commercial low cost, thin film solar cells. In this structure, CdS serves as a cheap window material [1] while direct bandgap (1.45 eV) CdTe is a good match to the solar spectrum. However, fabrication of cheap, high-efficient, large-area CdS-CdTe solar cells remains to be a rather difficult scientific and technological problem.

A variety of deposition techniques have been used to grow CdS films with desirable optical, electrical and structural properties, among them chemical deposition [4,5], physical vapor deposition [6,7], spray pyrolysis [8,9], and electrodeposition [10,11]. Each of the above-listed techniques has some advantages and disadvantages, and a cost/quality ratio may serve as an important criterion of selection. In this connection, method of screen printing with a subsequent sintering is one of the cheapest and convenient techniques for fabrication both of semiconductor layers and ohmic contacts [12, 13, 14]. Distinctive features of these techniques are its profitability and opportunity to prepare large area films. However, there is a problem to obtain planar homogeneous films with optimum structural and electrophysical parameters.

As it is known, thermal treatment is one of the basic technological methods for conversion of the systems to the state close to equilibrium or with a certain degree of deviation from equilibrium, but the choice of optimal conditions for thermal processing requires many efforts. Indeed, in the case of real semiconductors, especially for multilayer systems, recrystallization may be accompanied by many "secondary", frequently undesirable processes such as interdiffusion, formation of new phases and point defects, oxidation, macrostrain relaxation with formation of dislocations, etc. [15].

In the present paper, the results of studying the processes of structural ordering in screen- printed CdS polycrystalline films under various conditions of sintering are described. The practical aim of those investigations is to obtain films, structural and electrophysical parameters of which are suitable for fabrication of CdS/CdTe solar cells.

2. Experimental

The paste for screen printing of CdS layers was prepared by mixing the different w/w ratios of chemically precipitated CdS and $CdCl_2$ powders with propylene glycol as a binder. The paste was screen printed through a polyester screen onto glass substrate. The screen-printed films were sintered at various temperatures from 600 to 690 °C for 1, 1.5, 3 and 6 hours in argon atmosphere. Films of differ-

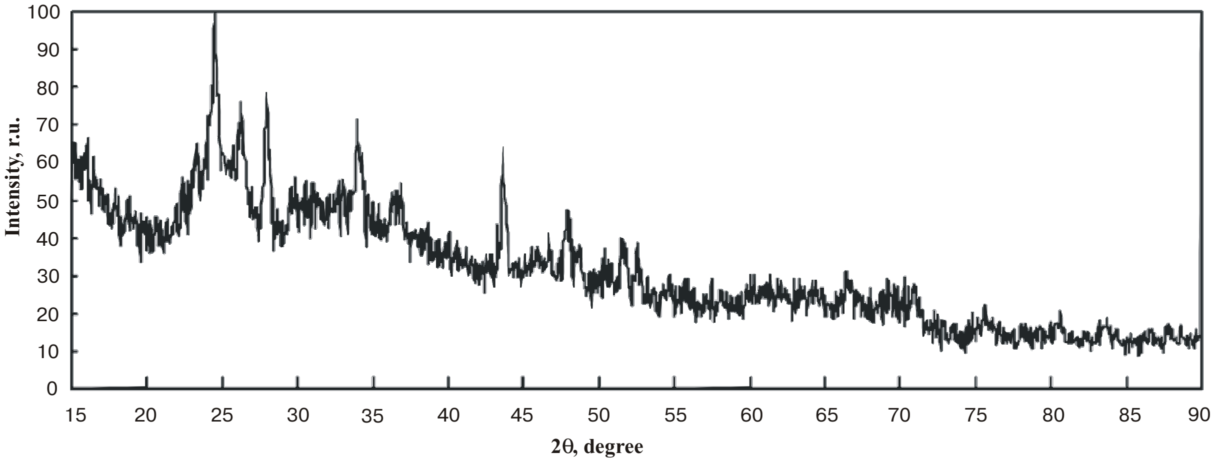


Fig. 1. XRD pattern of the CdS films screen-printed on a glass substrate and dried at a room temperature.

ent compositions were prepared by varying $CdCl_2$ to CdS ratio.

The uniformity of CdS film surfaces, transformation dynamics of grain size, the shape of the grains and changes in the grain boundaries at annealing were monitored by the optical microscopy (OM) methods. The structural analysis was done by studying X-ray diffraction (XRD) with DRON-3M diffractometer using Cu K_α radiation ($\lambda = 1.542$ A). The focusing LiF- monochromator was used in diffraction geometry in order to improve the sensitivity. The information concerning the phase composition of CdS films, averaged crystallite size and orientation, the level of micro- and macrostrains as well as behavior of structural defects was obtained from XRD data. Electrical properties were studied with a standard four-probe Van der Pauw method [16].

3. Results and discussion

To establish the specific features of sintering and recrystallization and to study solid-state chemical reactions in CdS films, a set of samples heat treated under different technological conditions were investigated.

The representative X-ray difractogram of the CdS films screen-printed on a glass substrate and dried at a room temperature, is shown in Fig. 1. As it is seen, the dried paste consists, basically, from hexagonal fine-dyspers CdS crystallites. At the same time, one can see the peak in the range of 34° angle that belongs neither to hexagonal nor to cubic CdS structures. It is difficult to identify this peak accurately, but it may be supposed that it corresponds to binding phases in the paste.

Heat treatment of the film within 1 h results in essential structural changes (Fig. 2a). The contribution of the amorphous X-ray (quasi-amorphous) phase decreases. This decrease is confirmed by a disappearance of smooth «tail» of the difractogram in the range of 15-20° angles. The formed weak and dim peak with a maximum at 17.5° is indicative of the residual quasi-amorphous phase, which is not recrystallized. An analysis of the phase structure of the film carried out on a basis of XRD measurements shows that the film consists of the hexagonal CdS phase with a prefered <100> orientation of the crystallites. Close to sharp Bragg peaks (25°), the wide range of the diffusive X-ray scattering (DXS) is observed, which is indicative of high density of defects inside the film. Note that we have not recorded extraneous phases in the films.

The increase both of temperature and heating duration up to 650 °C and 1.5 h, respectively, results in some structural changes. Particularly, microstrain and crystallite size rises. The crystallite size was evaluated from spreading of the diffraction peaks of different orders in the Cauchy approximation (Table 1) [17]:

$$f(2\theta) = \frac{K\lambda}{D\cos(\theta)} + 4\frac{\Delta d}{d}\mathrm{tg}(\theta)\,, \tag{1}$$

where θ is the Bragg angle, λ is the wave length of X-ray radiation, D is the crystallite size, Δd is the change of the interfacial distance, K is the factor depending on the nature and crystal structure of the material.

Table 1.

Duration and temperature of heating, h	Drying at 20°C for1.5	Heating at 600°C for 1	Heating at 650°C for 1.5
Crystallite size, nm	56	245	684

Increase of heating duration up to 3 h at temperature 650°C causes more essential rise in the crystallite size at lower microstrain level, without changes in the film texturing (Fig. 2b). Note that the DXS background is appreciably reduced. Simulation of the difractograms received (Fig. 3) shows that the best fit of the calculated and experimental ones can be obtained under assumption that 17 % of the film volume contains hexagonal CdS crystallites preferentially oriented along <100> axis. The rest part of the film is characterized by the

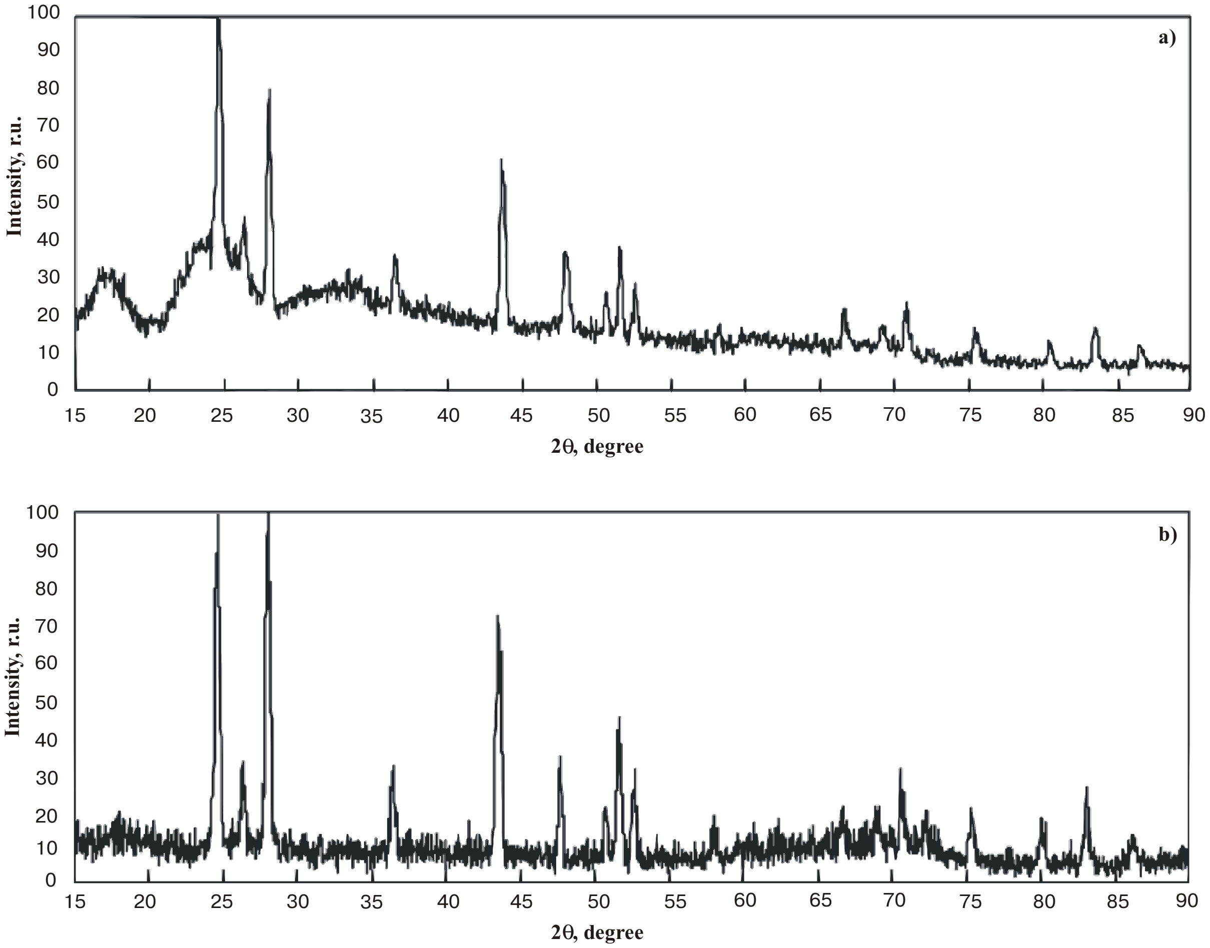


Fig. 2. XRD pattern of the CdS films sintered at 600°C for 1h (a) and 650°C for 3h.

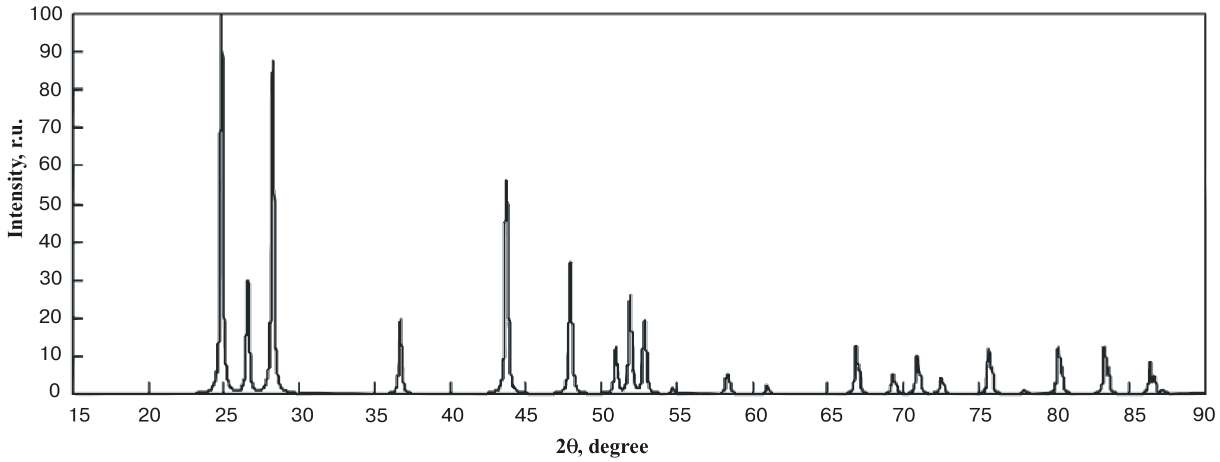
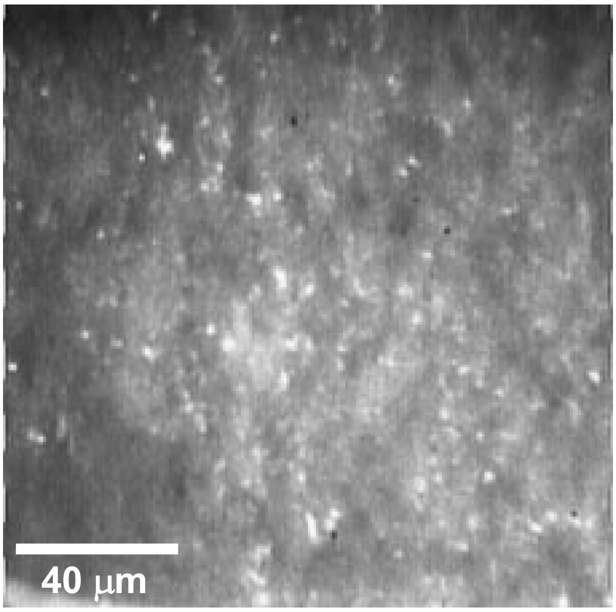
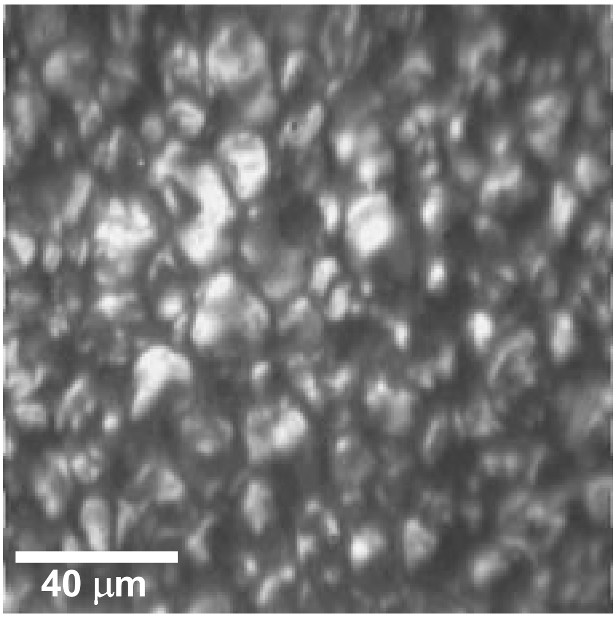


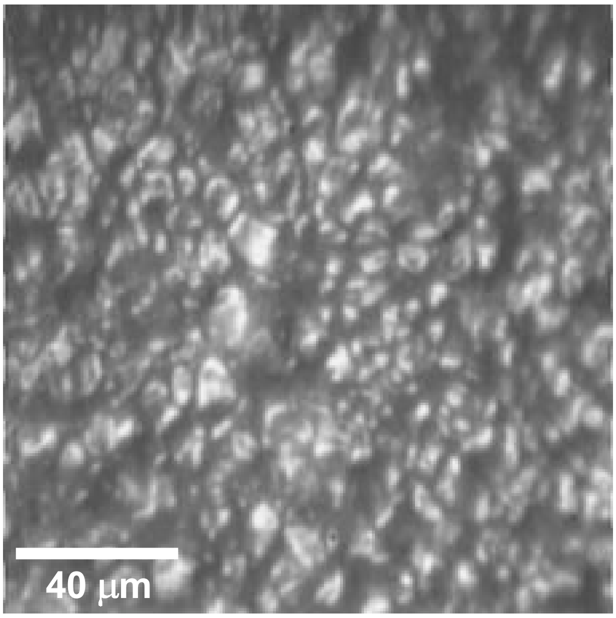
Fig. 3. Simulated diffractogram of CdS film. The best fit of the calculated and experimental patterns was obtained under assumption that 17 % of the film volume contains hexagonal CdS crystallites preferentially oriented along <100> axis.



(a)



(c)



(b)

Fig. 4. The changes of granularity of the film surfaces obtained by the optical microscopy method: dried paste CdS (a), CdS films sintered at 650°C for 1.5h (b) and 650°C for 3h (c).

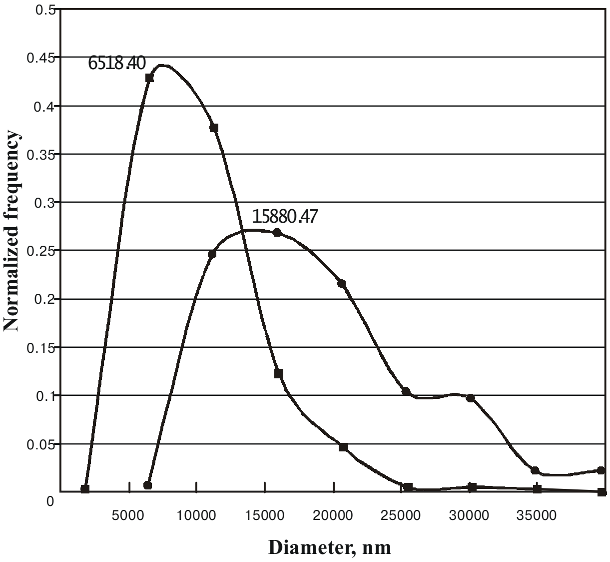


Fig. 5. Histograms of grain diameter distributions: CdS films sintered at 650°C for 1.5h (curve 1) and 650°C for 3h (curve 2).

equiprobable crystallite orientations along all directions (similarly to powders). Supposition about the presence of cubic phase in the CdS film does not give an acceptable fit of the calculated and experimental difractograms.

Fig. 4 illustrates the change of granularity of the film surface obtained by the optical microscopy method. It is seen that at heating duration within 3 h at temperature 650 °C, the surface grain size is twice increased as compared with heat treatment within 1.5 h, and the size scatter is smaller, though the cross size of some grains attains 40 microns (Fig. 5). At the same time, 120°-boundaries of grains appears. The fact that the average size of surface grains is by an order of magnitude higher than the average crystallite size (obtained from the OM measurements) shows that the process of grain coalescence is not still finished. In other words, the grains have been coagulated, but most of them have not got the same crystallographic orientation. Note that the large size of surface grains is particularly due to the fact that conditions for the grain growth are more favorable at the free surface rather than in the film volume.

To estimate qualitatively the dislocation density ρ_D at the interface of grains under definite conditions of film treatment, the following relation was used (under supposition that the volume of blocks is free of dislocations) [18]:

$$\rho_D = \frac{3n}{D^2}, \qquad (2)$$

where D is the grain size, n is the number of dislocations on each side (n = 1 at random distribution of dislocations). Dislocation density at the grain boundaries equals $4.8 \cdot 10^7$ cm^{-2}.

The microstrain values have been obtained by us from the analysis of spreading of the diffraction peaks. Those values have been determined in the direction normal to the film/substrate boundary. However, the microstrain values determined in the direction parallel to this boundary would be more important from the point of view of diagnostics of structure of the film as a whole. We have determined those latter values by the method of a sample revers (the so-called "sin2y method") [19]. The microstrain values have been defined from the difference between the interfacial distances d determined both in a perpendicular direction and at the angle y to the film surface:

$$\sigma_\varphi = \frac{E}{(1+\mu)\sin^2\psi} \cdot \frac{d_\psi - d_\perp}{d_\perp} \qquad (3)$$

where E and μ are the Young's modulus and Puasson's coefficient, respectively.

Dependences of the macrostrain level from temperature and heating duration are shown in Fig. 6. As seen, the macrostrain level is changed nonmonotomically. It is obvious that the processes of sintering pass in the screen-printed film at the first stages of heat treatment. Such processes show themselves in spontaneous material condensation (its transformation into a monolith) and in structural changes both of shape and orientation of crystallites. Process of condensation results in a significant increase of macrostrain. Indeed, the film is stretched, while the substrate is compressed. The fact that the structural transformations are not so intensive (small grains, low strain) at heating temperature 600°C may be explained by insufficient energy of thermal activation Q. The time interval τ before system transition to the thermodynamically more stable state begins, is reduced with increasing temperature T by exponential law [15]:

$$\tau = \tau_0 \exp\left(-Q/_{RT}\right). \qquad (4)$$

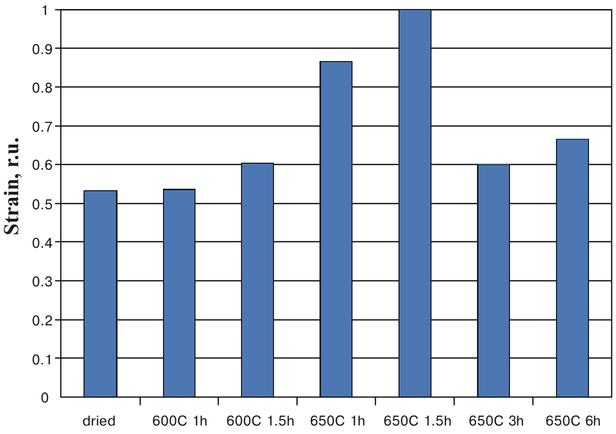


Fig. 6. Changes of macrostrain level under thermal treatments.

The increase of temperature up to 650°C makes above processes much more intensive. However, in this case the material condensation passes faster than the diffusive homogenization and relaxation of the stressed state. This process shows itself in a macrostrain peak observed at this temperature. It is necessary to note that the increase of heating temperature up to 690°C results in appearance of supercritical stresses as well as to destruction of CdS film due to formation of microcrack system.

It may be concluded from the macrostrain level and from the view of the grain surface after heat treatment of the film at 650 °C within 1.5 h (Fig. 4b), that the process of sintering is finished and the process of primary recrystallization passes. In the course of such recrystallization, the existing grains are transformed to another grains characterized by a higher level of crystal perfection, but the thermodynamic equilibrium is not still achieved.

An increase of the heating duration up to 3 h (at the same temperature) is sufficient for finishing the primary recrystallization and for a transition into a collective phase, where the scattering in grain sizes does not exceed 3-4 times and the grains are rather perfect. This is confirmed both by the decrease of the macrostrain level (Fig. 6), and by the practical disappearance of the diffuse «inflow» in the region of (100), (002) and (011) peaks (22-29° region), resulted from the intensive DXB on different structural defects in grains (Fig. 2b). Note that smearing of the peak at 17.5° connected with the presence of quasi-amorphous CdS phase, is also observed.

In the case of collective recrystallization the growth of grains stops on achievement of certain grain size. It is caused by reduction of driving force of migration of grain boundaries due to saturation of boundaries with different defects and to formation of equilibrium threefold joints of grains (i.e., of grains boundaries crossed at angle of 120° [15]). Just such a situation occurs after film heating within 6 h at 650°C. The grain size remains practically the same, as after 3-hours heating, but insignificant increase of a macrostrain level is observed. It can be connected with the change of equilibrium in the ensemble of point defects and dislocations at the grain boundaries.

4. Conclusions

It may be concluded from the results obtained that the heat treatment at 650°C for 3 h is an optimal regime for processing of screen-printed CdS films. Under those conditions, the grains attain their largest size at minimum macrostrain level. The films prepared are single-phase at preferred orientation of crystallites along <100> direction. Structural ordering of films passes in three stages, these are: sintering, primary recrystallization and collective recrystallization.

The homogeneous polycrystalline CdS films prepared by screen-printing method, have a sufficiently high optical transparency and low specific resistance. This allows one to use them as «windows» and conducting layers in photosensitive heterojunction structures.

Acknowledgents

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