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A Combined Sintering-Sublimation Method to Grow Light Responsive Polycrystalline Thin Films

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A combined sintering-sublimation method has been used to grow CdS or CdSeS photo-conducting polycrystalline thin films. By a fast firing technique, the films are grown on Cr_2O_{3-x} ceramic pellet sintered substrate. The film growing and the fast firing sintering processes take place simultaneously. The sintering-sublimation technique has been designed to increase the reliability of photo-conducting devices, mainly by decreasing the donors' concentration which determines a higher sensitivity. This process becomes more effective when pellets containing raw CdS, respectively CdSeS, and a less reactive component – such as nonstoichiometric chromium oxide, are used. This oxide provides surfaces where thin CdS or CdSeS layers are crystallizing. At the same time, the nonstoichiometric Cr_2O_{3-x} can react with the oxygen allowing a more efficient control of the properties of CdS and CdSeS thin layer which is generated as a result of the above-mentioned sublimation-condensation process.

Keywords: CdS and CdSeS photo-conducting devices; nonstoichiometric Cr_2O_{3-x}; sintering-sublimation technique

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INTRODUCTION

The sintering-sublimation technique has been designed to increase the reliability of photo-conducting devices mainly by decreasing the donor concentration which determines an elevated sensitivity. This method combines three different processes i.e., vacuum evaporation, thin layers growth from vapors and ceramic pellets sintering [1–3]. Previous observations have shown that when sintering CdS ceramic pellets, transparent, high purity monocrystals have been condensed on the cooler parts of the oven. This process becomes more effective if in the raw CdS another component is present with a limited reactivity, such as nonstoichiometric chromium oxide [3,4]. This oxide provides surfaces on which thin CdS (CdSeS) layers are crystallizing. At the same time, the nonstoichiometric Cr_2O_{3-x} can react with the oxygen allowing a more efficient control of the properties of the CdS thin layer generated as a result of the above mentioned sublimation-condensation process. A reductive atmosphere (a mixture of CO, CO_2 and N_2), specific to graphite crucibles, inhibits the further oxidation of CdS (CdSeS) films and thus improves their quality. This new method confers a high reliability photo-conducting A_2B_6 onto a porous ceramic Cr_2O_{3-x}. In this, way concomitantly to the pellets sintering, the sublimation – condensing transport of A_2B_6 is carried out.

A more detailed investigation concerning the influence of the growth conditions together with an additional improvement of the photo-conducting CdS (CdSeS) films could allow to elaborate a physical model of this process, both of them having a positive effect on the material manufacturing.

This article aims at presenting the modeling the growing process of thin photo-conducting CdS (CdSeS) layers by a sintering-sublimation technique. The experimental data obtained by optical methods are also presented, these being in agreement with the model proposed.

GROWTH PROCESS MODELING

In the case of AB type chalcogenide materials, the sublimation is usually followed by their dissociation to elemental compounds [5,6] according to the equation:

$$AB_{\text{solid}} \rightleftharpoons A_{\text{solid}} + \frac{1}{2}B_{2\text{gas}} \tag{1}$$

According to the mass action law, there is a simple relationship between the vapor total pressure p above the material and its absolute temperature T:

TABLE 1 The Values of the C_1 and C_2 Constants for A_2B_6 Considered Completely Dissociated in Gaseous Phase

A_2B_6	C_1	C_2	ΔT (K)
ZnS	13846	10.571	1095–1435
	13026	12.723	1482–1733
ZnSe	12340	9.051	980–1210
ZnTe	11513	9.718	918–1095
CdS	11564	10.137	902–1062
	11760	10.361	923–1427
CdSe	10848	9.461	1367–1513
CdTe	10030	9.740	829–1236
	9981.3	9.824	1085–1324

$$\log p = -C_1/T + C_2 \tag{2}$$

where the C_1 and C_2 constants have different values depending on material and temperature interval.

In the case of AB type chalcogenide materials, the C_1 and C_2 constants take the following values [5,6] (see Table 1).

In the references [7–9] the general conditions necessary for a molecule of chalcogenide compound to be fixed on a support are established. Based on these criteria, an experimental method known as the "Three temperatures principle" has been elaborated [8,9]. According to this principle, if the support temperature is higher than the sublimation temperatures T_A and T_B of both components, then on the support only the molecules of the AB chalcogenide are condensed.

In this case,

$$C_i = \frac{N_A}{\sigma_0 \sqrt{2\pi M_i R T_i}} e^{Q_i/RT_i} \tag{3}$$

where the Q_i is the activation energy for the synthesis of chalcogenide compound on the support and σ_o is the maximum number of atoms absorbed on the support.

MATERIALS AND METHODS

For the preparation of cadmium sulfide for optoelectronic purposes, cadmium salts, SCN_2H_4 and Na_2S are used as raw materials, and the strict control of pH, temperature and amount of water is need. The method for obtaining the sulfo-selenide of cadmium is based on two stages: the preparation of the solutions and the precipitation of the product. Such compounds of high purity have been obtained at

laboratory level. The impurity level is less than 20 ppm, and consists mainly of Zn, Fe, Mg, Mn, Cu, Ni and Co. The powder of CdS contains crystals of which 90% are between 2 and 4 μm, and CdSeS particles of which 95% are between 1 and 3 μm.

The scheme of the main operations contains: the synthesis and purification of the cadmium nitrate, the thiourea purification, the ammonia solution purification, the cadmium sulfide and the cadmium sulfide selenide synthesis.

Synthesis and Purification of the Cadmium Nitrate

In a polyethylene recipient, provided with a polyethylene stirrer, the deionized water, the cadmium R1 and the pure nitric acid are introduced.

After the end of reaction, the clear solution was decanted and cadmium oxide is added till the pH equals 4. Hydrogen peroxide and pure ammonium monocarbonate have been also added. The solution was stirred for two hours and was filtered on a Buchner vessel. In the solution warm to 60°C, purified ammonia solution 25% was added and boiled for 2 hours. After the cooling and filtering, a cadmium nitride 3 N solution was obtained, with 50 g/L cadmium ions.

The thiourea and ammonia solution have been also purified by standard procedures.

Cadmium Sulfide Synthesis

In a quartz glass recipient the 3 N cadmium nitride solution has been introduced while a 3 N thiourea solution was added under permanent stirring. After 3 hours of stirring at 60°C, the ammonia purified solution has been added and the solution was stirred at the same temperature for 7 hours. The clear solution was decanted and the precipitate was washed five times, decanted and filtered. The precipitate resulted was washed with deionized water until the total removal of nitrate ion (no more reaction with barium chloride). Finally the precipitate was filtered and washed with pure ethanol.

The drying of the precipitate was made in an electrical stove, for 24 hours, at the temperature of 120°C. The dried precipitate was grained in a triturator and heated for 10 hours in air, at 700–800°C, in an electric oven, provided with kanthal wire. After the cooling, the sample was milled and separated. The resulting cadmium sulfide had 3 N purity and average grain size between 30 and 65 μm.

A similar procedure has been applied for the synthesis of cadmium sulfide selenide.

The resulting cadmium sulfide selenide had 3 N purity grade and average size of grains between 10 and 65 μm.

TABLE 2 The Analysis of Impurities for Cadmium Sulfide Sample (1) and Cadmium Sulfide Selenide Samples (2 and 3)

Sample/Metal	Concentration, ppm						Total amount of imp (ppm)
	Fe	Zn	Mg	Cu	Co	Ni	
1	0.010	0.003	0.002	0.069	0.006	0.007	0.096
2	0.079	0.006	0.001	0.035	0.004	0.004	0.129
3	0.066	0.011	0.011	0.028	0.000	0.004	0.119

The analysis of impurities was made for three samples, one sample of cadmium sulfide (sample 1) and two for cadmium sulfide selenide (samples 2 and 3). The results are presented in the Table 2.

Thin Film Growth

The investigated thin polycrystalline films have been grown by using an installation similar to those used to grow monocrystals by the Bridgman method. It consists in a crucible made by nuclear graphite fixed on a road which executes an oscillating movement combined with a slow rotation (10 rpm) along the axis of a vertical oven. The distribution of the temperature along the oven axis is characterized by the presence of two steps corresponding to each extremities. Between these steps, the temperature increase monotonously with a medium gradient equal to $70^{\circ}C\,cm^{-1}$ (see Fig. 1).

The graphite crucible starts its vertical ascension at the middle of the low temperature threshold finishing it in the middle of the superior temperature, this movement being repeated during the entire thermal treatment varied between 10 minutes and 2 hours.

More details concerning materials preparation can be found in [3].

Optical measurements have been performed in polarized light by using a Leitz-Orthoplan-Pol Wetzlar microscope provided with a built-in photographic camera. Standard reticulated plates have been used to determine crystallite dimensions (see Fig. 2). As a result of the crucible displacement within the oven, transitory temperature gradients are generated both inside the pellets and between them. In this way during the pellets sintering, a sublimation - condensing transport of CdS (CdSeS) takes place. Thus displaced the pellets, CdS (CdSeS) vapors condensed on the cold faces of pallets by forming an optical pure polycrystalline layer whose crystallites dimensions depend on the thermal treatment chosen.

In our experimental setup, the pellets temperature is monotonously increasing from bottom (pellet no. 1) to top (pellet no. 10). By taking

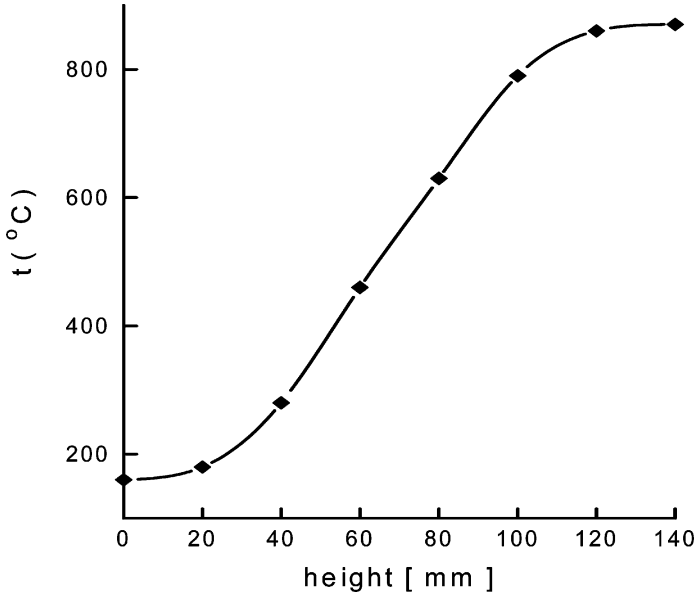

FIGURE 1 The vertical temperature distribution within the oven.

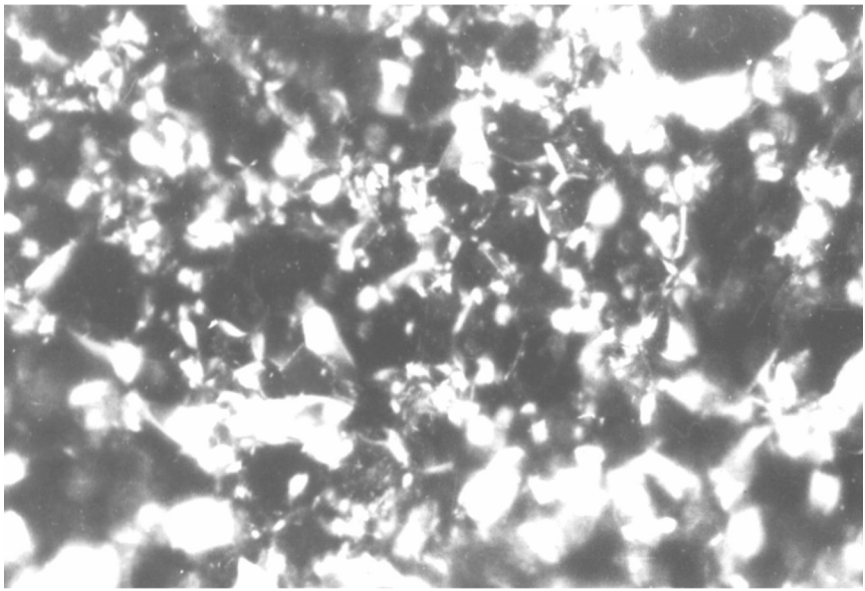

FIGURE 2 Polarized light image of a thin polycrystalline layer of CdS growth in the presence of nucleation. Average diameter of crystallites is equal to 50 μm (1 mm = 5 μm).

into account the Scholts and Klukow model [10], the following relationship between the functions *T(t)* which describe the time evolution of the Pellets temperatures can be written down:

$$\int_0^{\tau} T_1(t)dt < \int_0^{\tau} T_2(t)dt \cdots < \int_0^{\tau} T_{10}(t)dt \tag{4}$$

where τ represents the total time of the thermal treatment.

According to [10], only in the conditions described by Eq. (4) the thin layers of polycrystalline CdS (CdSeS) can be obtained. These layers are supported by a Cr_2O_{3-x} porous sintered pellet. The nonstoichiometric α-Cr_2O_{3-x} was obtained by quenching some quantities of Cr_2O_3 from 1100 K to reaction atmosphere. As a result, the α-Cr_2O_{3-x} which contained initially some oxygen vacancies was turned into a nonstoichiometric oxide.

The investigation of the nonstoichiometric α-Cr_2O_{3-x} have to establish an usual method for measuring the deviation from stoichiometry.

Electron Paramagnetic Resonance (EPR)

The Electron Paramagnetic Resonance (EPR) spectra have been recorded at room temperature of an X band JEOL, JES ME-3X

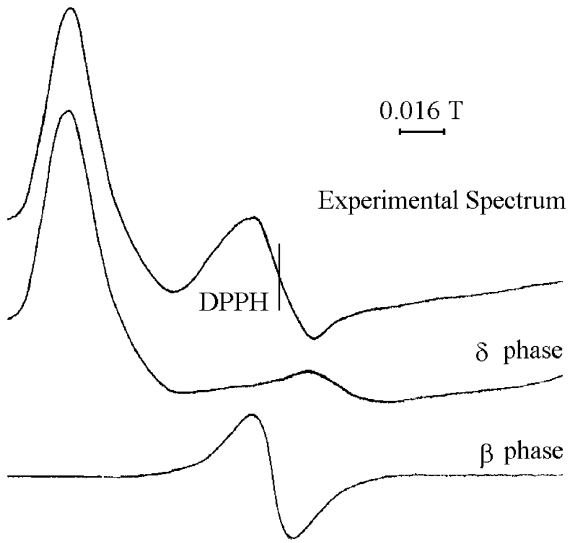

FIGURE 3 The experimental recorded EPR spectra of Cr_2O_{3-x} (upper) and the corresponding δ (middle) and β (lower) spectra as has been obtained by graphical de-convolution.

spectrometer. To obtain a better sensitivity, a 100 kHz modulation field has been used. DPPH was used as inner standard. Almost all the recorded spectra consisted of a superposition of two types of spectra (see Fig. 3). One of these spectra has shown only one symmetrical resonance Lorentz line. This type of spectrum, denoted by β phase is usually assigned to the clusters of Cr^{3+} paramagnetic ions. The second component of the experimental spectra had a characteristic shape for a paramagnetic center in an axial local symmetry. This spectrum known as δ phase, is typical for isolated Cr^{3+} ions spread onto entire volume of Cr_2O_3 [11]. The ratio R between the surface corresponding to δ phase and the surface corresponding to β phase is proportional to the deviation from the stoichiometry [12].

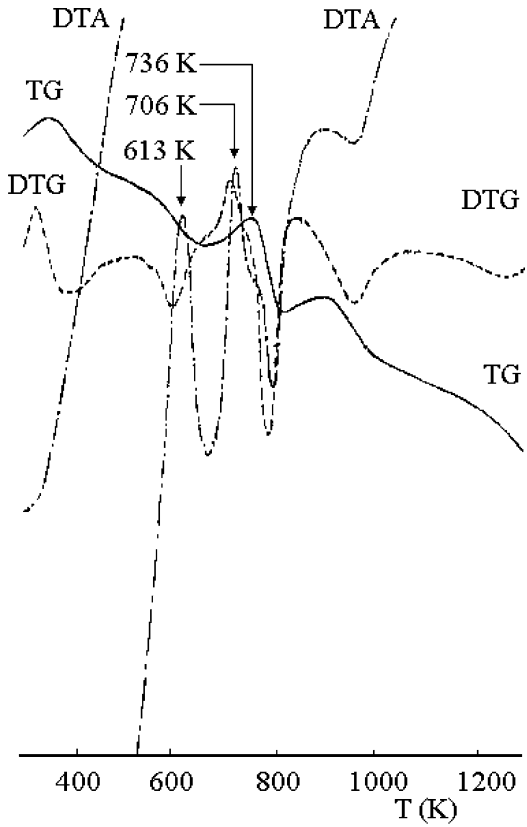

FIGURE 4 Thermal analysis for a sample of polycrystalline Cr_2O_{3-x}.

Differential Thermal Analysis (DTA)

The Differential Thermal Analysis (DTA) has been performed by using a Paulik MOM Budapest type derivatograph. The evaluation of oxidation-deoxidation kinetic parameter, produced in nonstoichiometric α-Cr_2O_{3-x} has been performed according to Coates-Redfern method. By analyzing the experimental DTA curves (see Fig. 4) it can be noticed the presence of two exothermic peaks. The first peak (613 K) can be attributed to an oxidation reaction while the second (706 K) is due to the generation of pollycrystalline Cr_2O_3 [13]. The peak of TG curve (836 K) can be explained by the oxygen chemosorbtion reaction:

$$2Cr_2O_3 + 3O_2 \rightleftharpoons 4CrO_3$$

By using the experimental DTA data, the deviation from stoichiometry has estimated [14]:

$$x \cong 0.52.$$

The activation of the photo-conduction in CdS (CdSeS) layers has been realized, depending on the layer thickness, by heating in air

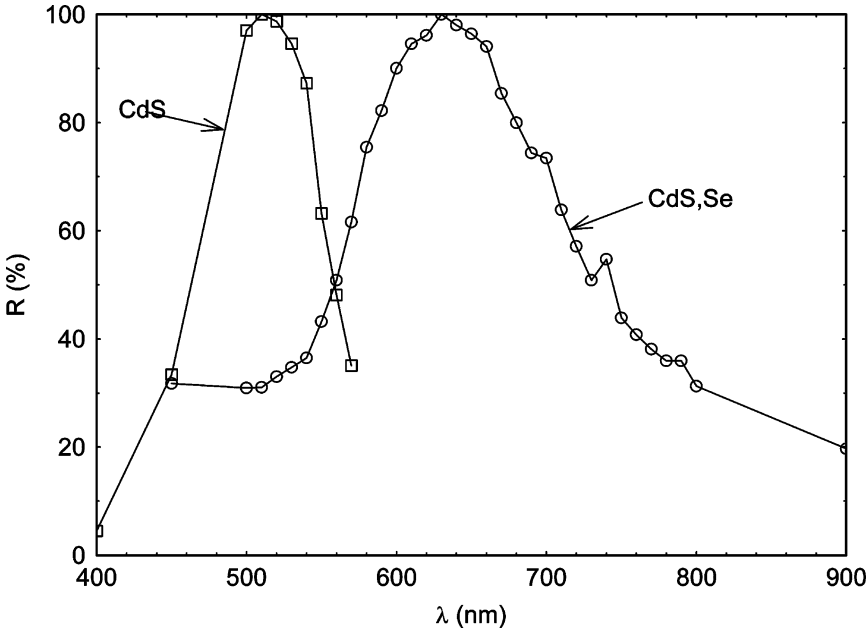

FIGURE 5 The spectral distribution of photo-conduction current for CdS:Cr_2O_3 and CdS,Se:Cr_2O_3.

for 5–10 min in the temperature range 600–700 K. The thermal treatment has been performed on an isothermal support in total darkness. In order to obtain electrodes, the final pellets have been sprayed by liquid tin through a mechanic mask by means of a CO_2 stream. The spectral distribution of Photoconduction Current (PCC) was determined by using a SPM 2 Zeiss type monochromator provided with a quartz prism and the entrance slit of 0.35 mm. The light source consisted of a Xenon type XBO101 lamp (100 W) and a set of neutral filters for attenuation of light. The intensity of PCC has been measured by using a Keithley 2000 multimeter, at room temperature. The samples were biased in an electric field of 0.2–4 V/mm. All the intensities measured have been normalized to the incident light intensity and maximum intensity of the photocurrent. One can see the displacement of the peak of PCC from 510 nm to 630 nm (see Fig. 5). The ratio of the dark resistance to the illumination resitance was $\sim 10^6$ ($CdS:Cr_2O_3$) and $\sim 7 \times 10^4$ ($CdS,Se:Cr_2O_3$).

CONCLUSION

By corroborating all these data the following remarks can be concluded.

New thin, polycrystalline photo-conducting layers have been prepared by using a combined sintering-sublimation method in the presence of nonstoichiometric α-Cr_2O_{3-x}.

When a solid solution CdS,Se [15] was used the displacement of the peak of PCC from 510 nm to 630 nm was carried out.

The presence of nonstoichiometric α-Cr_2O_{3-x} considerably influences the layer parameters acting as oxygen level regulator. According to [16] the activation of the photoconduction in CdS (CdSeS) layers has been produced during the thermal treatment in air resulting in a solid solution CdS (CdSeS)-CdO (0.1% mol.w). The presence of a less reactive component – such as nonstoichiometric chromium oxide has proven this behavior.

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