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# $A^{II}B^{VI}$ PHOTORESISTANCES BY SINTERING-SUBLIMATION TECHNICS

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The sintering-sublimation technics was conceived for increasing the reliability of the photoconductive devices, by decreasing the concentration of mobiles donors, which are utilised for photoconductive material sensibilisation. The technics combines three different technics: the vapor phase deposition; the vacuum vaporising; the ceramic sinterisation. This special technics gives stoichiometric layers. The technics avoids dissociation (the flash sublimation technic), sublimates the compounds from two different sources, on heated support, or sublimates the compound, with Cd excess. It was investigated, by mass spectrometry and optical absorption studies, the presence, in gaseous state, of the $A^{II}B^{VI}$ molecules. The condensation on the substrate of the vapors is difficult because the Cd, Zn and Hg elements have difficulties in the condensation process. The Frenkel model, of the condensation, can be successfully used for describing the process. This model uses the observations concerning the difficulty of the condensation on supports of those elements, at higher temperatures than 90 - 195 K. It is supposed that the support surface is a potential surface, with holes and potential walls, whose dimensions can not overcome the interatomic distances, for polished surfaces.

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## 1. Introduction

The photoconductive properties of chalcogenides and other materials are important for practical applications [1-4].

The sintering-sublimation technique has been designed to increase the reliability of photoconductive devices mainly by decreasing the donors concentration which determines a high sensitivity. This method combines three different processes i.e. vacuum evaporation, thin layers growth from vapors and ceramic pellets sintering. Previous observations have shown that when sintering CdS ceramic pellets, transparent, high purity monocrystals condense on the cooler parts of the oven. This process becomes more effective if there are used pellets containing together with the raw CdS another component, presenting a limited reactivity, 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-condensing process. A reductive atmosphere (a mixture of CO, $CO_2$ and $N_2$), specific to graphite crucibles, inhibits a further oxidation of CdS (CdSeS) films and thus improves significantly their quality. That new method produces high reliability photo conducting $A^{II}B^{VI}$ material onto a porous

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ceramic $Cr_2O_{3-x}$. In this way, together with the pellets sintering, take place the sublimation - condensing transport of $A_2B_6$.

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

In this paper it is presented an attempt of the modeling of the growing process of thin photoconductive CdS (CdSeS) layers by a sintering-sublimation technique. At the same time are presented the experimental data obtained by optical methods which are in agreement with the proposed model.

## 2. 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:

$$AB_{solid} \Leftrightarrow A_{solid} + ½\, B_{2\,gas} \qquad (1)$$

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

$$log\ p = -\,{}^{K_1}\!/_{T} + K_2 \qquad (2)$$

where the $K_1$ and $K_2$ constants take different values as function of material and temperature interval.

In the case of AB type chalcogenide materials, the $K_1$ and $K_2$ constants which take the values in table 1 [5,6].

Table 1. Numerical values of the $K_1$ and $K_2$ constants for $A_2$ $B_6$ considered completely dissociated in gaseous phase.

| $A_2B_6$ compound | Numerical values of the $K_1$ and $K_2$ constants | | Temperature interval (K) |
|---|---|---|---|
| | $K_1$ | $K_2$ | |
| 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 |

## 3. Experimental

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

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

After the reaction stopped, the clear solution was decanted and it was added cadmium oxide till the pH equals 4. It was added oxygenated water and pure ammonium monocarbonate. The solution was stirred for two hours and filtered on a Buchner apparatus. The solution was electrically heated to 60 $^oC$. In the warm solution it was added purified ammonia solution 25% and it was boiled for 2 hours. After the cooling the solution was filtered. It was obtained a cadmium nitride 3N solution, with 50 g/l cadmium ions.

In a quartz glass recipient it was introduced deionized water, and pure thiourea, under mechanical stirring. The solution was heated on an electrical plate to 60 °C. In the warm solution it was introduced purified zinc sulfate solution and 25% ammonia solution and it was boiled for 4 hours. After the cooling the solution was filtered and it was added deionized water. It was obtained a thiourea solution of 3N purity.

The purification of ammonia solution was made by several distillations of pure ammonia solution of 25% concentration, the vapors being captured in cooled deionized water.

In a quartz glass recipient it was introduced the 3N cadmium nitride solution. The solution was heated to 60 °C, after that it was introduced, under permanently stirring conditions, the 3N thiourea solution. After 3 hours of stirring, it was added the ammonia purified solution. 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 resulted precipitate was washed with deionized water until the total removal of nitrate ion (no more reaction with barium chloride). After that 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 furnace, provided with kanthal wire. After the cooling, the sample was milled and separated. The resulting cadmium sulfide had 3N purity and average grain size between 30 and 65 microns.

Cadmium nitrate 3N solution was introduced in a quartz glass recipient. The solution was heated to 75 °C and it was added, under stirring, a solution of selenium in 3N thiourea. After 4 hours of stirring it was added purified ammonia solution, under continuous stirring. The solution was boiled and stirred another 8 hours, adding each hour deionized water. The clear solution was decanted and the precipitate was washed 10 times with deionized water, filtered and washed again until the total removal of the nitrate ion (no more reaction with barium chloride). The precipitate was washed with pure sodium chloride solution, filtered and washed with pure ethanol. The precipitate was thereafter dried for 24 hours, at 120 °C. The dried precipitate was grained, heated to 800°C and maintained for 2 hours at this temperature. The sample was cooled and milled in a ball mill. The resulting cadmium sulfide selenide had 3N purity grade and average size of grains between 10 and 65 microns.

The impurities analysis was carried out for three samples, one sample of cadmium sulfide (sample 1) and two of cadmium sulfide selenide (sample 2 and 3) – see also [7]. The analysis results are presented in Table 2.

Table 2. The impurities analysis for cadmium sulfide sample (1) and cadmium sulfide selenide samples (2 and 3).

| Sample/ Metal concentration (ppm) | Fe | Zn | Mg | Cu | Co | Ni | Total amount of imp (ppm) |
|---|---|---|---|---|---|---|---|
| 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 |

In the references [8-10] it has been established the general conditions necessary for a molecule of chalcogenide compound to be fixed on a support. Based on these criteria, an experimental method known as the “three temperatures principle” has been elaborated [9,10]. 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 it will condense only the molecules of the AB chalcogenide. In this case,

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

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

The rate of thin film growth, in accordance with Shalimova&Voronkov's model [8] is:

$$\omega = Cp_0^2 \tag{4}$$

with: ω: the rate of thin film growth and $p_0$: the pressure of AB chalcogenide vapors.

## 4. The 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 of 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 extremity. Between these steps, the temperature increase monotonously with a medium gradient equal to 70 $^{o}$C cm$^{-1}$.

The graphite crucible starts its vertical ascension at the middle of the low temperature threshold finishing it in the middle of the superior one, this movement being repeated during the entire thermal treatment whose time moving varied between 10 minutes and 1/2 hour.

More details concerning materials preparation can be found in ref. [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 the crystallite size (see Fig. 1,2). As a result of the crucible displacement within the oven, transitory temperature gradients are generated inside the pellets as well as between them. In this, way together with the pellets sintering, sublimation - condensing transport of CdS (CdSeS) takes pace. Thus displaced, CdS (CdSeS) sinters on the cold faces of pellets by forming an optically pure polycrystalline layer whose crystallites dimensions depend on the chosen thermal treatment.

## 5. Results and disscutions

In our experimental setup, the temperature of the pellets monotonously increased from bottom (pellet no. 1) to top (pellet no. 10). Thus, by taking into account the Scholts and Klukow model [11], the following relationship between the functions T(t) which describe the time evolution of the pellets temperatures can be written down:

$$\int_0^\tau T_1(t)dt < \int_0^\tau T_2(t)dt .... < \int_0^\tau T_{10}(t)dt \tag{5}$$

where τ represents the total time of the thermal treatment.

According to [11], only in the conditions described by eq. (5) thin layers of polycrystalline CdS(CdSeS) can be obtained.

These layers are sustained by a $Cr_2O_{3-x}$ porous sintered pellet. The non-stoichiometric α- $Cr_2O_{3-x}$ was obtained by quenching from 1100 K of some quantities of $Cr_2O_3$ in reactive atmosphere. As a result, the α- $Cr_2O_{3-x}$ which contained initially some oxygen vacancies was turned into a non-stoichiometric oxide.

The activation of the photoconduction in CdS(CdSeS) layers has been realized, depending on of the layer thickness, by heating in air for 5 - 10 min. at a temperature in the range 600-700 K.

The thermal treatment has been performed isothermally in total darkness. On the final pellets, in order to obtain electrodes, we have sprayed liquid tin through a mask by means of a $CO_2$ stream. The spectral distribution of photoconduction current was determined by using a SPM 2 Zeiss type monochromator provided with a quartz prism and an entrance slit of 0.35 mm. The light source consisted of a Xenon type XBO lamp (100 W) and a set of neutral filters for attenuation of light was used. The intensity of PCC have been measured with a Keithley 2000 multimeter, at the room temperature. The samples were biased in an electric field of 0.2 - 4 V/mm.

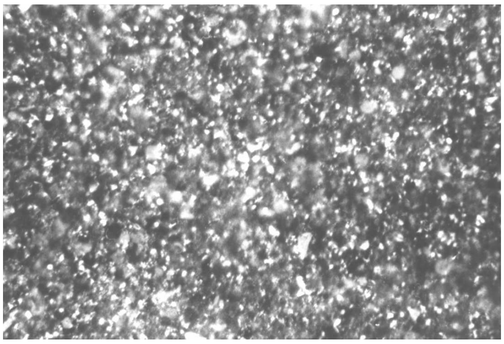

Fig. 1. Polarized light image of a thin polycrystalline layer of CdS growth at 1000 K. Average diameter of crystallites is equal to 5  (μm (1mm = 5μm).

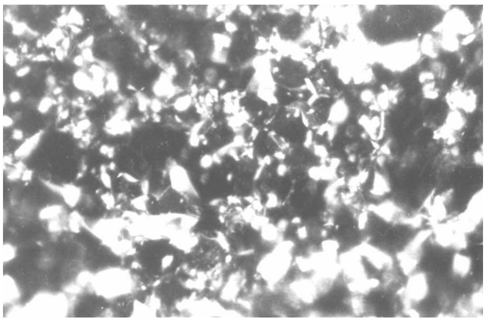

Fig. 2. Polarized light image of a thin polycrystalline layer of CdS growth at 1100 K. Average diameter of crystallites is equal to 80 μm (1 mm = 5 μm).

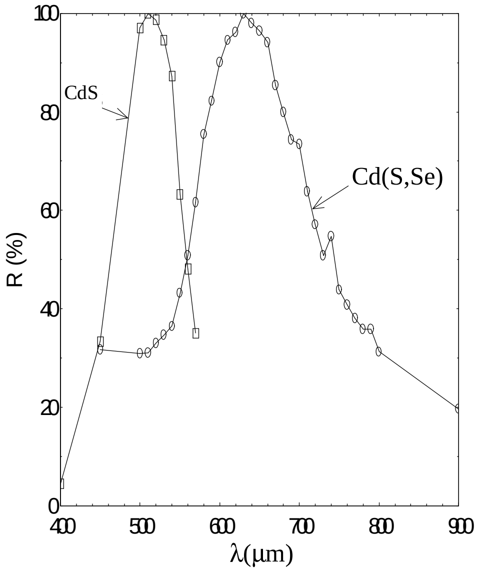

Fig. 3. The spectral distribution of photoconduction current  for $CdS:Cr_2O_3$ and $Cd(S,Se):Cr_2O_{3-x}$.

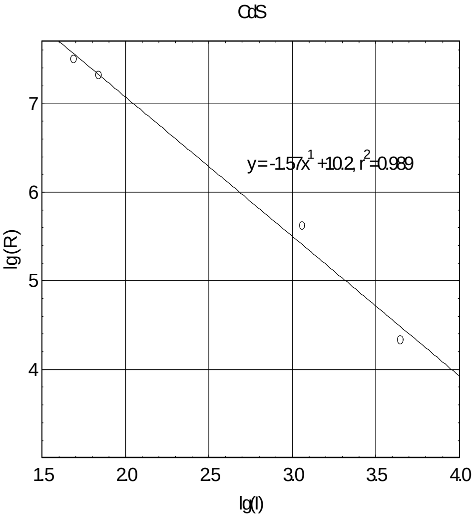

Fig. 4. The dependence of resistance on illumination for $CdS:Cr_2O_{3-x}$.

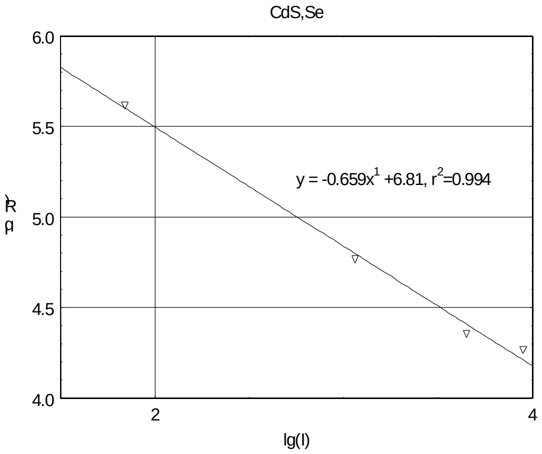

Fig. 5. The dependence of illumination resistance for CdSSe:$Cr_2O_{3-x}$.

All the measured intensities have been normalised 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. 3). The ratio of the dark resistance to the illumination resistance was ~ $10^6$ (CdS:$Cr_2O_3$) and ~$7\times10^4$ (CdS,Se:$Cr_2O_3$).

## 6. Conclusions

By using a combined method we were able to prepare thin, polycrystalline photoconducting layers in the presence of non-stoichiometric $\alpha$- $Cr_2O_{3-x}$.

By using a solid solution Cd(S,Se) we have obtained the displacement of the peak of PCC from 510 nm to 630 nm.

The presence of non-stoichiometric $\alpha$-$Cr_2O_{3-x}$ considerably influences the film parameters acting as oxygen level regulator.

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