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## Grain boundary conductivity in different polycrystalline MoSe<sub>2</sub> thin films

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**Abstract.** — It has been shown early that curved plots for the conductivity of polycrystalline diselenide molybdenum were systematically obtained whatever the technique used for the obtention of the layers. In the general case of polycrystalline semiconductors these deviations from the simple thermoionic emission across the grain boundaries have been recently attributed to potential fluctuations at the grain boundaries. Here a good agreement between the experimental results and this new theory is obtained. The result deduced from theoretical propositions is conformed by the scanning electron micrographs of the layers and other preceding experimental studies. In the light of the discussion of the MoSe<sub>2</sub> layers, a quality factor  $Q$  is proposed for photovoltaic thin films. This estimation shows that the films obtained by solid state reaction and substitution are the best. Mo and Te thin films are sequentially deposited. Then an annealing under Se and Te pressure at 770 K for 24 h gives crystallized and stoichiometric MoSe<sub>2</sub> thin films. These films have the higher quality factor among the films studied here ( $Q = 0.75$ ). This is in close agreement with the good electrical and optical properties of these layers.

### 1. Introduction.

The conductivity of polycrystalline semiconducting MoSe<sub>2</sub> thin films depend sensitively on the grain boundaries that is to say on the potential barriers and space charge regions that are built up around them. A strong temperature dependence of conductances is observed. We have analyzed this dependence with the [1-4] model of thermal carrier emission across grain boundary barriers. Therefore, temperature dependence of the conductivity is expected to yield straight lines in Arrhenius plots [5-8]. However this is not true in the whole temperature range, since the Arrhenius plot are systematically curved [1-4]. This deviation, more pronounced in the low temperature range has been discussed in term of deviations from the simple thermal emission theory. Two processes of conduction which operate simultaneously have been proposed. The thermoionic emission through the intergrain barrier which is dominant at higher temperatures ( $T \geq 250$  K) and the variable range hopping in the forbidden band of the grain which is preponderant at low temperature ( $T < 200$  K) [1-4].

Recently a new contribution has shown that the Arrhenius plots must be curved due to potential fluctuations at the grain boundaries [9].

The author has shown that these inhomogeneities at the grain boundary barriers due to statistically distributed interface charges result in curved conductivity plots for polycrystalline semiconductors, even if thermal carrier emission across barriers is the only current transport process.

We have previously described some new techniques to obtain MoSe<sub>2</sub> thin films [1-4]. Among the results obtained the conductivity data of these MoSe<sub>2</sub> films are used here to check the possibility of the model. A study by scanning electron microscopy is used to correlate the theoretical results with the homogeneity of the layers. Also earlier results [1-4] are recalled for the present discussion.

## 2. Film preparation and characterization.

The substrates are polished glass chemically cleaned and out gassed *in situ* prior to deposition by heating at 400 K for 1 h. The substrate temperature is controlled by a copper/constantan thermocouple attached by silver paste to sample surface. Four different techniques have been used to obtain MoSe<sub>2</sub> thin films in order to improve the crystalline quality of the films.

In a first time MoSe<sub>2</sub> thin films have been obtained by d.c. diode sputtering of pressed MoSe<sub>2</sub> powder [1]. These films which are amorphous and poor in selenium are post annealed. A first annealing under Se pressure at 770 K for 24 h followed by a second annealing under dynamic vacuum at 670 K for 24 h gives crystallized and stoichiometric MoSe<sub>2</sub> thin films. These films will be called « MoSe<sub>2</sub> sputtered layers 1 » in the following of the paper.

These films being poorly oriented, in order to optimize the texturation and therefore to improve the electrical properties of the films, MoSe<sub>2</sub> layers have been obtained by solid state reactions between Mo and Se thin films. Mo and Se thin films are sequentially deposited [3]. A first annealing under Se pressure at 770 K for 24 h followed by a second annealing under dynamic vacuum at 670 K for 24 h gives crystallized and stoichiometric MoSe<sub>2</sub> layers which will be called « MoSe<sub>2</sub> synthesized layers 1 ». This technique improves the electrical properties but not the orientation of the layers.

At the same time, MoTe<sub>2</sub> textured films were obtained by d.c. diode sputtering and post annealing [10]. Therefore, in order to improve the orientation of the sputtered MoSe<sub>2</sub> layers, a Se substitution technique has been used. After d.c. diode sputtering of pressed MoTe<sub>2</sub> powder the MoTe thin films obtained [2] were amorphous and poor in Te. They were annealed under Se and Te pressure for 24 h at 840 K and then they were post annealed under vacuum at 670 K for 24 h. When the atomic ratio Se/Te during the first annealing is more than 1.2, stoichiometric textured MoSe<sub>2</sub> films are obtained. These textured MoSe<sub>2</sub> films will be called « MoSe<sub>2</sub> sputtered layers 2 ».

A study of the electrical properties of these last layers has shown that the orientation improvement of the crystallites do not involve an increase of the electrical conductivity. So we have transferred this process to obtain MoSe<sub>2</sub> thin textured films by solid state reaction [4]. First Mo and Te thin films are sequentially deposited. Then an annealing under Se and Te pressure at 770 K for 24 h gives crystallized and stoichiometric MoSe<sub>2</sub> thin films which will be called « MoSe<sub>2</sub> synthesized layers 2 ».

For electrical measurement gold electrodes have been evaporated on MoSe<sub>2</sub> layers. Gold was chosen because gold thin films guarantee a good ohmic contact. An electrometer (Keithley 617) was used to measure the film d.c. conductance between 80 K and 700 K. The morphology and roughness of the film surface was visualized by scanning electron microscopy. The scanning electron micrographs were obtained using the 6400 JEOL field emission scanning electron microscope (SEM).

### 3. Experimental results.

The typical temperature dependence of the conductivity between 80 to 700 K for all the kinds of samples is shown in figure 1. It can be seen that in this temperature range, the resistivity does not follow an Arrhenius dependence, the samples exhibiting marked variations in  $\frac{\partial \ln \sigma/T}{\partial T}$  with temperature. The observed slopes are always increasing with the temperature which is, as discussed before, compatible with grain boundary scattering mechanisms.

It can be seen in table I that the ambient conductivity of the films increases when they are

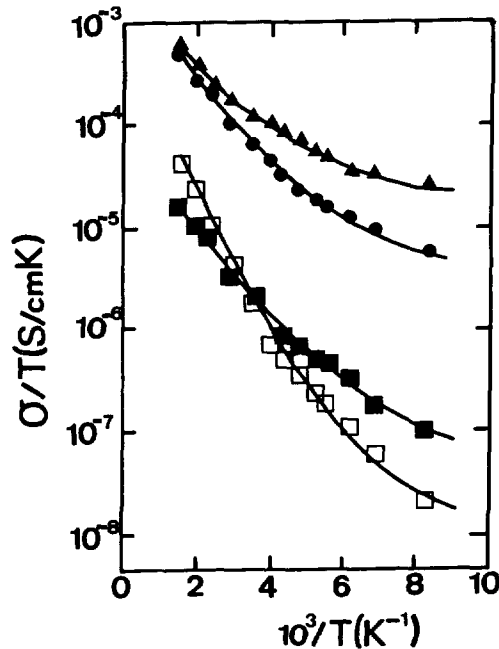


Fig. 1. — Temperature dependence of the conductivity. (■) MoSe<sub>2</sub> sputtered layers 1, (□) MoSe<sub>2</sub> sputtered layers 2, (▲) MoSe<sub>2</sub> synthesized layers 1, (●) MoSe<sub>2</sub> synthesized layers 2.

Table I. — Orientation, electrical and optical properties of MoSe<sub>2</sub> thin films.

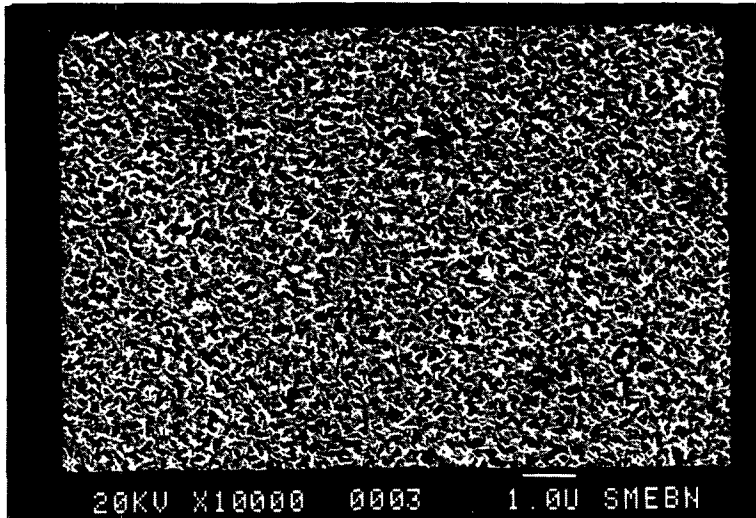
Sample	$\sigma_{300K} (\Omega\text{cm})^{-1}$	$E_{gTF}$	$F_{00\ell}$
MoSe <sub>2</sub> sputtered layer 1	$10^{-3}$	1.1 - 1.28	0.7
MoSe <sub>2</sub> sputtered layer 2	$10^{-3} - 10^{-2}$	1.39 - 1.49	1
MoSe <sub>2</sub> synthesized layer 1	0.15	0.9 - 1.14	0.8
MoSe <sub>2</sub> synthesized layer 2	0.1	1.17 - 1.25	1

$\sigma_{300K}$  room temperature conductivity,  $E_{gTF}$  optical gap,  $F_{00\ell}$  percentage of crystallites with their  $c$  axis perpendicular to the plane of the substrate. MoSe<sub>2</sub> single crystal:  $\sigma_{300K} = 1.4 (\Omega\text{cm})^{-1}$  (12);  $E_g = 1.17$  V (11).

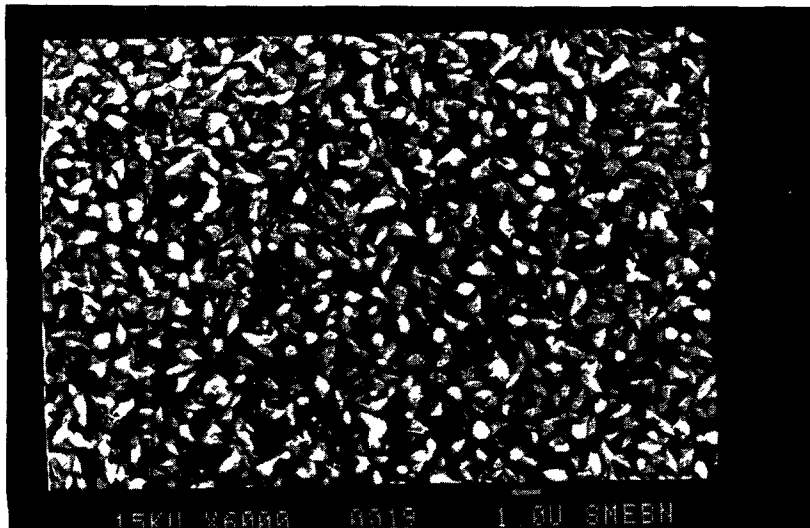
obtained by the solid state reaction. Table I gives also physical parameters deduced from earlier measurements [1-4] :

- the orientation of the crystallites has been deduced from X ray diffraction measurements ;
- the band gap has been estimated from the optical density of two films with different thicknesses.

The typical micrographs of the surface of the films are shown in figure 2. It can be seen that the  $\text{MoSe}_2$  sputtered layers 1 exhibit a quite lamellar structure (Fig. 2a). In the  $\text{MoSe}_2$  sputtered layers 2 the grains are greater than those obtained with the preceding method but the surface of

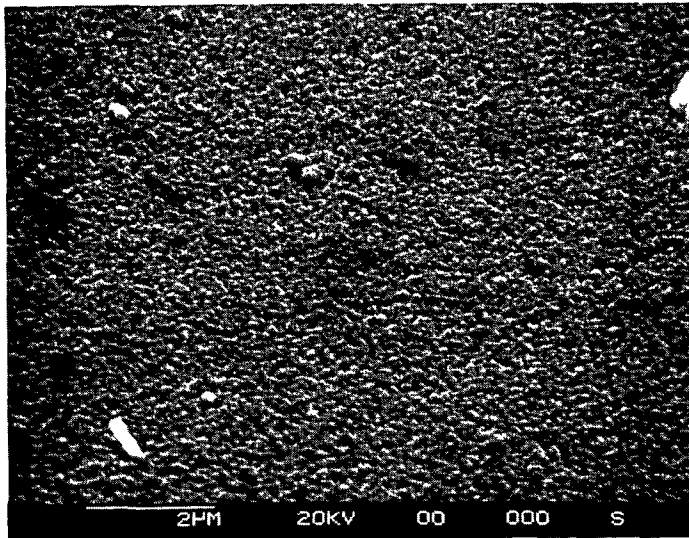


a)

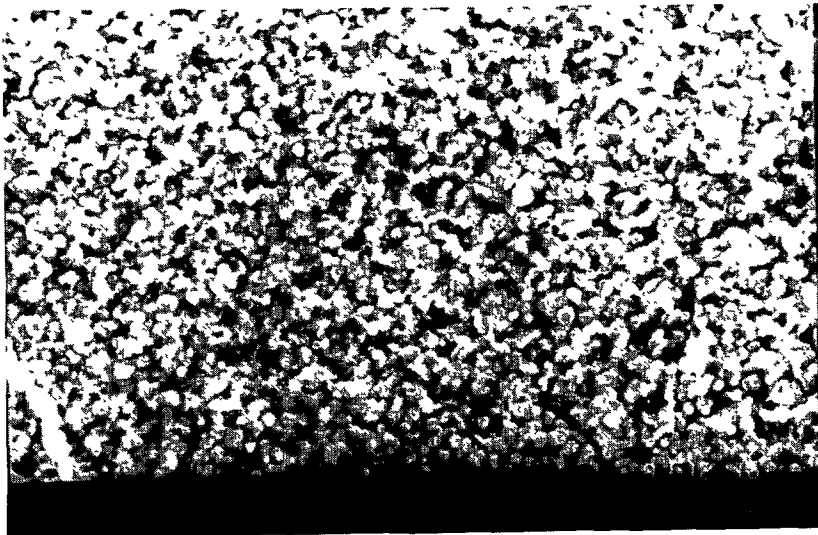


b)

Fig. 2. — Micrographs of the surface of the films. a)  $\text{MoSe}_2$  sputtered layers 1, b)  $\text{MoSe}_2$  sputtered layers 2, c)  $\text{MoSe}_2$  synthesized layers 1, d)  $\text{MoSe}_2$  synthesized layers 2.



c)



d)

Fig. 2 (continued).

the film is quite rough (Fig. 2b). The MoSe<sub>2</sub> synthesized layers 1 surfaces are homogeneous and smooth but the grain size is quite small (Fig. 2c). The grain size and the orientation of the crystallites increase in the case of the MoSe<sub>2</sub> synthesized layers 2 but the homogeneity of the surface decreases (Fig. 2d).

#### 4. Discussion.

In our previous papers the conductivity curves were not in agreement with the theoretical curves all along the temperature range studied. Therefore, while the high temperature range

was discussed in terms of grain boundary scattering mechanisms, the low temperature range was usually discussed in terms of variable range hopping [1-4].

The classical thermal emission across grain boundary [7] is given by (1) :

$$J = A^* T^2 e^{-q\zeta/kT} e^{-qV_{gb}/kT} (1 - e^{-qV_d/kT}) \quad (1)$$

with :  $A^*$  effective Richardson constant,  $kT/q$  thermal energy,  $q\zeta$  Fermi level position within the grain :  $q\zeta = E_C - E_F = kT \ln(N_c/n)$ ,  $N_c$  effective density of state,  $n$  carriers density,  $V_{gb}$  barrier potential at the grain boundary,  $V_d$  bias voltage.

As shown by Werner [9] if we introduce potential variations among different boundaries and model the fluctuating barrier  $\phi$  by a Gaussian distribution :

$$P(\phi) = \frac{1}{\sigma_\phi \sqrt{2\pi}} e^{-(\bar{\Phi} - \phi)^2 / (2\sigma_\phi^2)} \quad (2)$$

with  $\bar{\Phi}$  mean barrier,  $\sigma_\phi$  standard deviation.

We obtain

$$\phi_{\text{eff}}(T) = \bar{\Phi}(T) - \frac{\sigma_\phi^2}{2kT/q} \quad (3)$$

It can be seen that  $\phi_{\text{eff}}$  decreases upon cooling. The slopes of Arrhenius plots of conductivities are therefore curved upwards.

Werner has shown that the temperature dependent activation energy  $E_{\text{act}}$  (in Fig. 1) is given by :

$$E_{\text{act}}(T) = -k \frac{d}{dT^{-1}} \ln(\sigma_{\text{gb}}/T) = q \left( \bar{\Phi}(T=0) - \frac{\sigma_\phi^2}{kT/q} \right). \quad (4)$$

Therefore validity of the model need that the curves of figure 1 can be described by a parabola. In that case the activation energy  $E_{\text{act}}$  of the Arrhenius plot for  $\sigma_{\text{gb}}/T$  varies linearly with  $T^{-1}$ . The plot of  $E_{\text{act}}$  versus  $T^{-1}$  has an y-axis intercept of  $q\bar{\Phi}(T=0)$  and yields  $\sigma_\phi$  from the slope.

It can be seen in figure 1 that a good agreement between the experimental points and parabola is obtained. The curves deduced from the derivative of the parabola are reported in figure 3. The corresponding values obtained for  $\bar{\Phi}$  and  $\sigma_\phi$  are reported in table II. The MoSe<sub>2</sub> sputtered layer 1 present reasonable  $\bar{\Phi}$  and  $\sigma_\phi$  but the room temperature conductivity  $\sigma_{300\text{K}}$  is very small. This is probably tied to the poor orientation of crystallites ( $F_{00\ell} = 0.7$ ) and to their small size, which is corroborated by the microphotograph of figure 2a. While the MoSe<sub>2</sub> sputtered layer 2 are textured ( $F_{00\ell} = 1$ ) they are quite resistives, the values of  $\bar{\Phi}$  and  $\sigma_\phi$  are the worst of the layers studied here. This is in good agreement with the anormously high value of  $E_g$  which have been attributed to the very rough surface of the layers [2] as shown in figure 2b. Here also the high values of  $\bar{\Phi}$  and  $\sigma_\phi$  can be attributed to this large roughness and to the inhomogeneity of the films.

The differences between the synthesized films are not so large. The two kinds of samples have a far higher conductivity than the sputtered samples. Their electrical properties are quite similar. The value of the band gap of the MoSe<sub>2</sub> synthesized layer 2 is identical to the value measured for a single crystal [11], this fact can be attributed to the better crystallisation of this films (Tab. I, Figs. 2c, d).

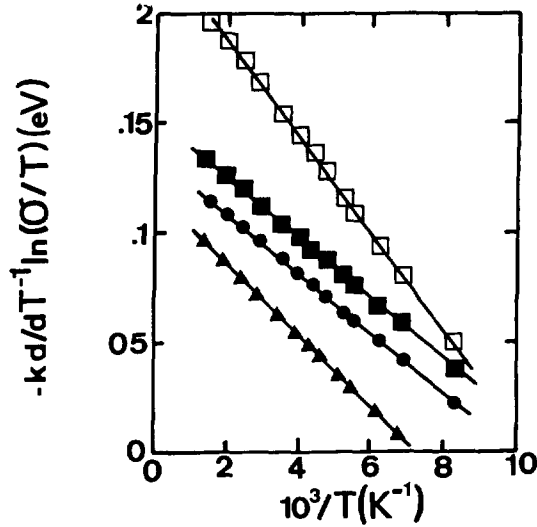


Fig. 3. — Slope of the curved plots from figure 1. (■) MoSe<sub>2</sub> sputtered layers 1, (□) MoSe<sub>2</sub> sputtered layers 2, (▲) MoSe<sub>2</sub> synthesized layers 1, (●) MoSe<sub>2</sub> synthesized layers 2.

Table II. — Physical parameters deduced from plots of figure 3, homogeneity and quality factors.

Sample	$\sigma_{300K} (\Omega cm)^{-1}$	$q\bar{\phi} (eV)$	$\sigma_{\phi} (mV)$	H	Q
MoSe <sub>2</sub> sputtered layer 1	10 <sup>-3</sup>	0.15	13	11.5	0.001
MoSe <sub>2</sub> sputtered layer 2	10 <sup>-3</sup> - 10 <sup>-2</sup>	0.23	22	10.45	0.05
MoSe <sub>2</sub> synthesized layer 1	0.15	0.12	16	7.5	0.44
MoSe <sub>2</sub> synthesized layer 2	0.1	0.13	13	10	0.75

The discussion above has shown that the knowledge of  $\bar{\phi}$  and  $\sigma_{\phi}$  is very interesting in order to estimate the quality of the films and their homogeneity. The results can be easily understood in the light of X-ray diffraction and scanning electron microscopy studies. The discussion above has shown that the obtention of textured films with large grain size is not sufficient to obtain good quality films (cf. MoSe<sub>2</sub> sputtered films 2). We have reported in table II the homogeneity factor proposed by Werner to qualify the polycrystalline films [9]. It can be seen that, if H is able to estimate the homogeneity of the films, we need a more restricting quality factor when these films should also have their electrical and optical properties as near as possible to those of a single crystal. Therefore the estimation of the quality of the films need to take into account their conductivity and their band gap. For a polycrystalline film we propose a quality factor Q such that :

$$Q = \frac{\sigma_{TF}}{\sigma_{SC}} H \left( 1 - \frac{|E_{gTF} - E_{g0}|}{E_{g0}} \right)$$



$\sigma_{TF}$ ,  $E_{gTF}$  thin film conductivity and optical band gap.  $\sigma_{SC}$ ,  $E_{g0}$  conductivity and optical band gap of the single crystal. (In stoichiometric polycrystalline films we have always  $\sigma_{TF} < \sigma_{SC}$ ).  $H$  homogeneity factor proposed by Werner such that  $H = \bar{\Phi}(T=0)/\sigma_{\phi}$ . The highest is  $Q$ , the highest is the quality of the films.

In the present study the films of  $\text{MoSe}_2$  obtained by substitution of Se in  $\text{MoTe}_2$  synthesized films ( $\text{MoSe}_2$  synthesized films 2) are the best ones.

## 5. Conclusion.

Conductivity previously understood in terms of grain boundary and variable range hopping can be understood by using the model of grain boundary potential fluctuation described by Werner [9]. We have shown, by studying different kinds of  $\text{MoSe}_2$  layers, that this simplification allows also a good estimation of the homogeneity of the films. The values found for the mean potential and its fluctuations are in the same order for all the layers excepted for the  $\text{MoSe}_2$  sputtered layer 2.

The estimation of the quality of the films compound requires the knowledge of its conductivity and its band gap. In the present study the films of  $\text{MoSe}_2$  obtained by substitution of Se in  $\text{MoSe}_2$  synthesized films ( $\text{MoSe}_2$  synthesized films 2) are the better one for solar cells application.

The discussion presented here will be now broaden to other films of the same family obtained in our laboratory and also in other laboratories. This could give a good estimation of the possibility of each kind of films for solar cells application.

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