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## Optical and Electrical Properties of CuAlSe<sub>2</sub> Thin Films Obtained by Selenization of Cu/Al/Cu...Al/Cu Layers Sequentially Deposited

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Optical and electrical properties of CuAlSe<sub>2</sub> thin films obtained by selenization of Cu/Al/Cu...Al/Cu layers sequentially deposited have been investigated. It is shown that the expected energy gap (2.67 eV) is measured for well crystallized films, whereas a slightly higher value is measured for films not so well crystallized. Raman diffusion also shows differences between well and poorly crystallized films with peaks corresponding to the reference powder for the former samples. A p-type conductivity is found whatever the crystalline quality of the samples. The conductivity of the films depends also strongly on their crystalline properties. When the films are badly crystallized their conductivity is controlled by highly disordered domains at the grain boundaries. When the films are well crystallized with (112) texturation the room temperature conductivity of the films is three orders of magnitude higher than that of poorly crystallized films. Moreover, in the high temperature range, the different domains of the plot  $\ln(\sigma)$  versus  $(1/T)$  can be understood by using single crystal models, which demonstrates the high crystalline quality of the films. In the lower temperature range, the conductivity is governed by grain boundary scattering mechanisms.

### 1. Introduction

Recently great attention has been paid to the properties of CuAlX<sub>2</sub> (X = Te, Se, S) due to their technological interest. These I–III–VI<sub>2</sub> ternary chalcopyrite compounds have a large band gap ( $E_{g\text{CuAlTe}_2} \approx 2.1$  eV [1],  $E_{g\text{CuAlSe}_2} \approx 2.7$  eV [2],  $E_{g\text{CuAlS}_2} \approx 3.5$  eV [3]), and can be used as window buffer layer in photovoltaic devices especially with other photoconductive ternary chalcopyrite compounds. These films can be p-type or n-type [4]. Recently we have depicted a new simple technique to obtain CuAlSe<sub>2</sub> thin films [5]. In this paper we report their optical and electrical properties.

### 2. Experimental

#### 2.1 Thin film preparation

The depositions were done in a vacuum of  $10^{-4}$  Pa. The substrates were soda-lime glass chemically cleaned and outgassed in situ prior to deposition by heating at 400 K during 1 h. The substrate temperature during deposition was 400 K. Cu, Al and Se of 99.999% purity were used. Cu and Al were deposited by alternate thermal evaporation from two tungsten crucibles. The evaporation rate (0.2 nm/s for Cu and 0.2 nm/s for Al) and the film thicknesses were measured in-situ by a hf quartz monitor. A rotating substrate holder allows to put alternatively the samples above the different crucibles. The layer

thicknesses were calculated to achieve the desired composition and varied from 10 to 15 nm. The number of layers varied from 5 to 15 for each component. The upper layer was a Cu layer to prevent Al oxidation. The atomic ratio was  $\text{Cu/Al} = 1.1 \text{ at}\%$  since it has been shown that Cu excess improves the crystalline quality of the I–III–VI<sub>2</sub> chalcopyrite compounds [6]. The  $\text{CuAlSe}_2$  films were then synthesized by selenization of the Al/Cu/Al...Al/Cu sequence. The samples were introduced with a small amount (0.1 to 5 mg) of selenium in a vacuum sealed Pyrex tube.

Then this tube was annealed for 24 h at 823 K. After cooling it has been shown [5] that it was necessary:

– to anneal the samples under dynamic vacuum, to sublimate the selenium condensed at the surface of the layer during the cooling of the tube;

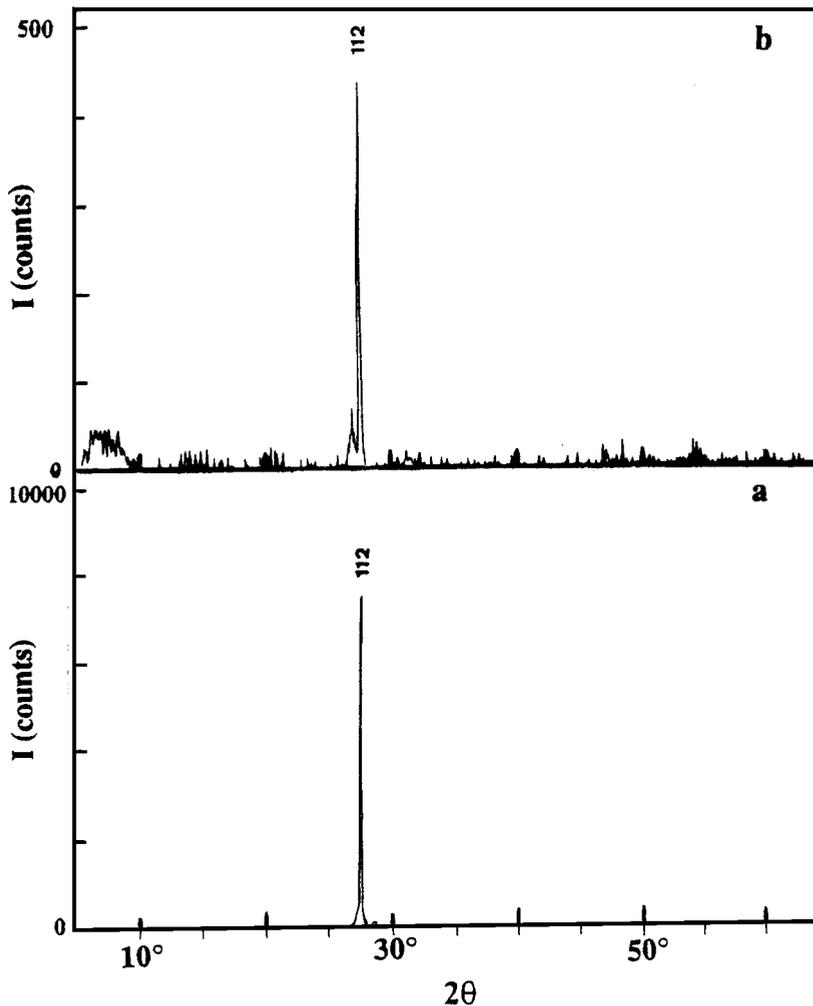


Fig. 1. X-ray diffraction spectra for  $\text{CuAlSe}_2$  thin films of different crystalline quality: a) well crystallized, b) badly crystallized

– to etch chemically the samples in a 0.1M KCN liquid solution to etch the Cu<sub>2-δ</sub>Se grown at the surface.

At the end of the process, CuAlSe<sub>2</sub> films were obtained with different crystalline quality, depending on the Se atmosphere provided during the annealing (Fig. 1). It has been shown earlier that a higher Se atmosphere during annealing induces a better crystallization of the thin films [7]. In this work, we effectively observe that the multilayer structures annealed under higher Se pressure (it means the biggest mass for the same volume) give the better films.

## 2.2 Characterization technique

The structure of the films has been checked using an analytical X-ray system type DIFRACT AT V3 Siemens instrument which uses the graphics program EVA. The wavelength was 0.15406 nm. The optical measurements were carried out at room temperature using a Cary 2300 spectrophotometer. The optical density was measured between 400 and 2000 nm. The absorption coefficient  $\alpha$  has been calculated from the measured transmission  $T$  of two samples of different thicknesses. Any errors occurring in the values due to uncertainties induced by this technique are much less than the errors in the thickness measurements which dominate the experimental errors.

For electrical measurements metal electrodes were evaporated after CuAlSe<sub>2</sub> synthesis. Gold was selected because gold thin films gave a good ohmic contact. The film ac conductance was measured with an electrometer (Keithley 627) between 290 and 550 K.

The sign of the majority carriers has been checked by the hot probe technique.

## 3. Experimental Results

As foreseen, the crystallization quality of the films varies with the selenium pressure during the annealing. This selenium pressure was at least 10<sup>3</sup> Pa and at maximum 10<sup>5</sup> Pa. To simplify, only the extreme results are discussed below even if a lot of intermediate results have been obtained.

### 3.1 Optical properties

CuAlSe<sub>2</sub> is a direct gap semiconductor [2]. For an allowed direct band gap transition the absorption coefficient  $\alpha$  can be related to the photon energy  $h\nu$  by

$$(ah\nu)^2 = A(h\nu - E_g),$$

where  $A$  is a constant and  $E_g$  is the energy gap. Therefore, for a direct band gap semiconductor, the  $(ah\nu)^2$  versus  $h\nu$  characteristic is predicted to be a straight line with a photoenergy axis intercept indicating the band gap. This is illustrated in Fig. 2 for different crystalline qualities. The room temperature data indicate direct band gaps of about 2.67 eV. This is in good agreement with the values measured in single crystals [2] and in epitaxial layers [8]. Nevertheless for the poorly crystallized films, the band gap is slightly higher. This broadening of the band gap is classically obtained when the disorder increases [9]. Moreover, if we cannot exclude an exponential nature of the absorption edge of the well crystallized films of CuAlSe<sub>2</sub> (Fig. 2, curve a), the poorly crystallized films exhibit not only exponential nature of the absorption edge but also a large absorption below this edge (Fig. 2, curve b). It has been shown that, although such Urbach tail

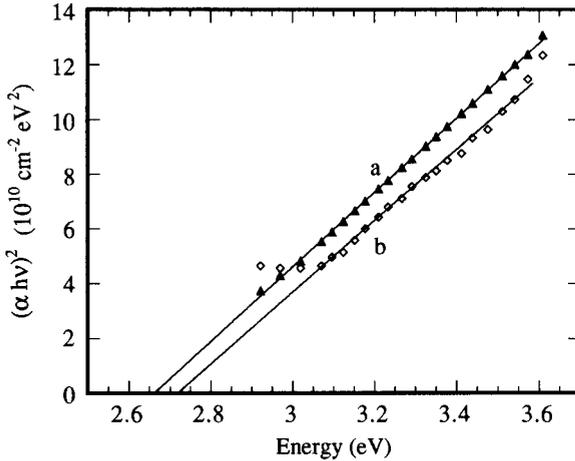


Fig. 2. Optical absorption for  $\text{CuAlSe}_2$  thin films of different crystalline quality: a) well crystallized, b) badly crystallized

is not unusual in single crystals [10], an exponential shape of the fundamental absorption edge occurs in semiconductors in the presence of a sufficiently high concentration of lattice defects [10]. Therefore the effect visible in Fig. 2 should be related to differences in the crystalline quality of the samples.

### 3.2 Raman diffusion

For Raman diffusion, we can also observe a great difference between the two types of films (Fig. 3a and b). If we compare these spectra with the reference powder spectrum (Fig. 3c) we can see that the well crystallized films exhibit exactly the same peaks as those of the reference powder. It must be noticed that the peaks correspond to those described in the literature [11].

In the case of the poorly crystallized film, we only observe the two main peaks of  $\text{CuAlSe}_2$  at  $184$  and  $234 \text{ cm}^{-1}$  showing that a  $\text{CuAlSe}_2$  film of lower crystalline quality has been synthesized.

### 3.3 Electrical properties

The carrier type has been determined by the hot probe technique. It has been shown that all the films are p-type, a result which has already been found by Chichibu et al. [12].

The room temperature conductivity of the films depends strongly on their crystalline quality. For thin films having the same thickness (200 nm) the room temperature conductivity increases by three orders of magnitude when the intensity of the (112) X-ray diffraction peak is multiplied by twenty. Conductivity measurements performed on typical  $\text{CuAlSe}_2$  thin films are given in Fig. 4. The results are plotted as  $\ln(\sigma)$  versus  $10^3/T$ . Here also two characteristic behaviours are presented.

In the case of poorly crystallized films (Fig. 4, curve b) the conductivity is small, the activation energy increases more or less with the reciprocal temperature. Since these films are poorly crystallized, the grains are “bathed” in a disordered grain boundary matrix sufficient to dominate the conductivity. The conductivity is controlled by the grain boundaries and/or amorphous domains between the crystallites.

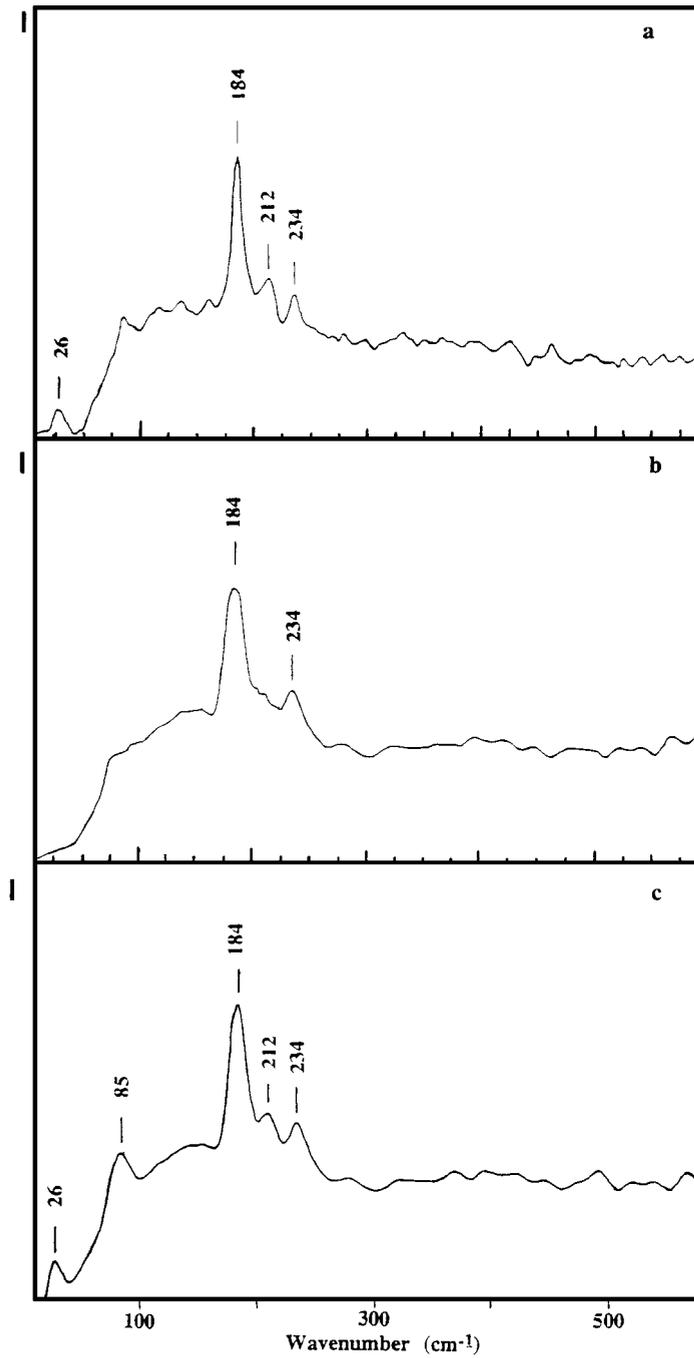


Fig. 3. Raman spectra for  $\text{CuAlSe}_2$ : a) well crystallized, b) badly crystallized, c) reference powder

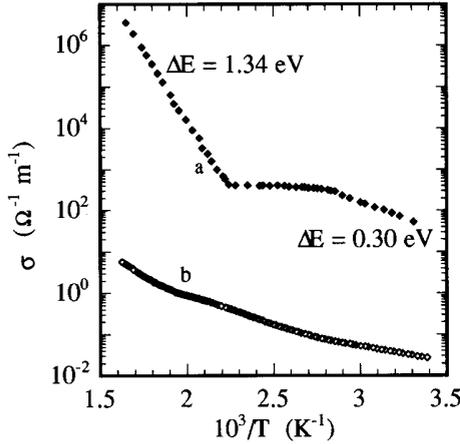


Fig. 4. Electrical conductivity for  $\text{CuAlSe}_2$  thin films of different crystalline quality: (a) well crystallized, (b) badly crystallized

In the case of well crystallized films (Fig. 4, curve a) the  $\ln(\sigma)$  versus  $10^3/T$  shows three quasi-linear regions:

- in the high temperature limit the activation energy is 1.34 eV which is the activation energy for the creation of holes and electrons in the valence and conduction bands since  $E_g = 2.7$  eV, this domain is the intrinsic domain;
- in the low temperature range an activation energy of 0.30 eV is obtained which may correspond to the ionization domain but also to grain boundary scattering mechanisms. This will be discussed below;
- between these two domains the activation energy is nearly zero which may correspond to the saturation domain.

#### 4. Discussion

In the case of poorly crystallized films their properties are controlled by the grain boundaries which are broad, highly disordered domains. In the case of textured films the optical and electrical properties are nearly the same as those of single crystals. However, for the temperature domain below 310 K the dominating phenomenon should be discussed.

The activation energy ( $2\Delta E = 0.60$  eV) deduced from the slope of the low temperature range of curve a of Fig. 4 can be attributed to an energy level introduced in the band gap by some defect or impurity [12 to 14]. However, such a large ionization energy has never been measured in this ternary compound and the variation of the activation energy with the crystalline state of the sample is difficult to explain.

Another possibility in this temperature domain is that the conductivity is governed by grain boundary scattering. Often in polycrystalline films the conductivity is controlled by the grain boundaries. The grain boundary trapping theory assumes that the grain boundaries are highly disordered resistive domains with trapping states, which capture free carriers and therefore make them immobile [15, 16]. These charged states at the grain boundary create depleted regions (of thickness  $W$ ) and potential barriers which hinder the passage of carriers from a grain (of length  $L$ ) to the neighbouring ones. Therefore, as shown in Fig. 5 for the polycrystalline trapping model, the resistance  $R$  and the resistivity  $\rho$  are given by

$$R = (R_1 + R_2) \rightarrow \rho = \rho_1 \left(1 - \frac{2W}{L}\right) + \rho_2 \left(\frac{2W}{L}\right).$$

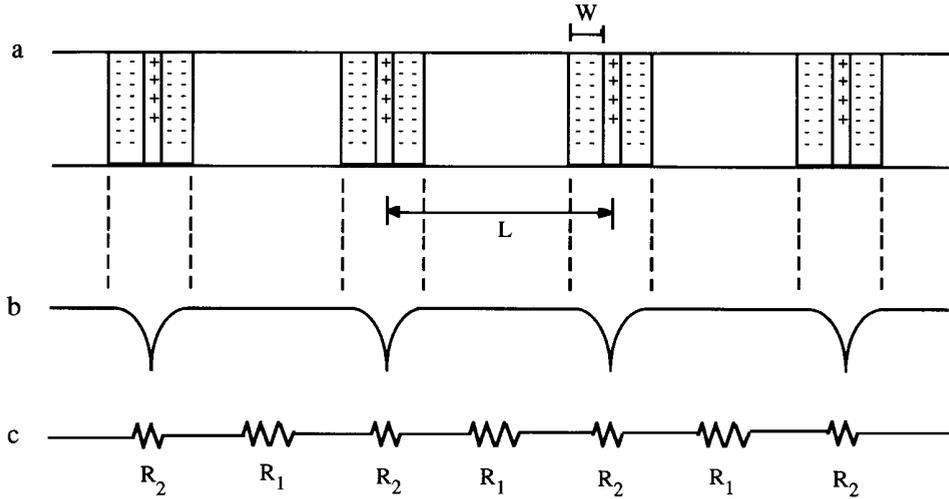


Fig. 5. Polycrystalline trapping model: a) one-dimensional grain structure, b) band bending for partially depleted grains, c) equivalent schematic resistance

It is well known that in the high temperature range, the conductivity is often no longer limited by the grains [17, 18]. In this temperature range, the energy of the free carriers is high enough to activate the carriers beyond the barrier and electrons are excited in the extended state of the conduction band. Therefore, theoretically the thermal energy gap should be estimated from the slope  $\Delta E$ . The value obtained in the present work (2.68 eV) is in good agreement with the optical gap (2.7 eV). At intermediate temperatures in the saturation domain  $\Delta E$  should be nearly zero. This is also the result obtained, see Fig. 4, curve a.

In the low temperature range the large activation energy which cannot be explained by defect ionization can be attributed to a grain boundary process, which means that in this temperature range, the grain boundary effect becomes prominent in these films [17].

In the case of poorly crystallized samples the activation energy increases with the temperature. It has been shown [19] that in the case of fluctuating barrier height at the grain boundary, the plot of  $\ln(\sigma) = f(1/T)$  does not follow an Arrhenius law but a parabola.

It can be concluded that the well crystallized films not only follow the conductivity laws of the single crystal in the high temperature range but also that the films are homogeneous with homogeneous barrier height at the grain boundary. This is not the case in the poorly crystallized films. Here, not only the grain boundaries are dominating all over the temperature domain studied, but also the barrier height at the grain boundary varies, they are not homogeneous.

The difference between the activation energy of well crystallized sample (0.30 eV) and that of the worse sample (0.62 eV) can be understood by introducing the theoretical barrier height value  $\Phi_B$  at the grain boundaries given by Seto [15],

$$\Phi_B \approx q \frac{Q_t^2}{8\epsilon N},$$

where  $q$  is the electron charge,  $Q_t$  the trap density in the grain boundary,  $\epsilon$  the dielectric constant and  $N$  the majority carrier density.

The density of traps decreases in the grain boundaries when the crystalline quality of the film is improved, which explains the variation of  $\Phi_B$ .

It has already been shown that annealing under higher selenium pressure improves the structural and electrical properties of CuInSe<sub>2</sub> films [20]. These authors have shown that the presence of selenium further improves dramatically the recrystallization and electronic properties of the films, which improves the performances of solar cells due to this treatment. They propose that a sintering effect involving elemental selenium, as for instance liquid phase surrounding the CIS grains and promoting the coalescence between the grains by liquid phase sintering occurs. At high Se pressure the recrystallization is more important due to a higher mobility of the grains. The same process probably occurs in our CuAlSe<sub>2</sub> films.

## 5. Conclusion

It is shown that the electrical and optical properties of CuAlSe<sub>2</sub> films obtained by selenization of Cu/Al/Cu...Al/Cu sequentially deposited layers depends strongly on the crystalline properties of the films.

Large disordered grain boundary domains control the properties of poorly crystallized films. The properties of highly textured films can be interpreted by using mainly models developed for the CuAlSe<sub>2</sub> single crystals which shows the high quality of these films. However, there is some difficulty to obtain reproducible results. It appears that the selenium pressure during annealing is not the only important parameter to obtain well crystallized films. The nature of the substrate is also very important. The first results obtained on tin oxide coated glass have shown that CuAlSe<sub>2</sub> films with high crystalline properties are systematically obtained, which is very promising for the future.

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