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$CuAlSe_2$ Thin Films Obtained by Chalcogenization (*)

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Abstract. — $CuAlSe_2$ thin films have been synthesized by chalcogenization of thin Cu and Al layers sequentially deposited by evaporation under vacuum. It is shown that $CuAlSe_2$ films are obtained with some $Cu_{2-\delta}Se$ and Se phases present at the surface These surface phases are suppressed by annealing under vacuum and by chemical etching in a KCN solution. At the end of the process, the XRD spectrum demonstrates that textured $CuAlSe_2$ films have been obtained with preferential orientation of the crystallites along the (112) direction. The gap of the films is 2.7 eV as expected. The films are nearly stoichiometric, but their surface is quite rough The XPS spectra show that some Na diffuses from the substrate toward the surface during the annealing process. However, this Na is etched by KCN.

1. Introduction

Ternary $I-III-VI_2$ chalcopyrite semiconductors have received considerable attention in recent years because of their applications in photovoltaic devices.

If the $CuInSe_2$ is the most extensively studied compound of the family, some other ternary chalcopyrites have attracted much attention on recent years because of large potential applications. Among them, $CuAlSe_2$, which is a large band gap material – $Eg = 2.67 eV$ [1] – can be used as an emitting layer of a blue light photoelectroluminescent devices or as a window in heterostructures photovoltaic devices. If for the former application heteroepitaxial films are needed, in the case of the latter application polycrystalline films can be used.

In this paper, we describe a very simple and cheap technique which allows to obtain well crystallized $CuAlSe_2$ polycrystalline thin films ; some attempts have been done also with $CuAlTe_2$.

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2. Experimental Techniques

$CuAlSe_2$ films were obtained by chalcogenization (annealing under selenium atmosphere of Cu/Al/Cu...Al/Cu thin layers sequentially deposited).

The substrates were polished soda lime glass or silicon, chemically cleaned. Then the substrates were out gased "*in situ*" prior to deposition by heating to 400 K for 2 h. The Cu and Al films were deposited in vacuum (pressure 5×10^{-4} Pa) by evaporation from two tungsten crucibles. The purity of Al was 99.99%, that of Cu was 99.999% and that of Se was 99.999%. Layers of Cu and Al were deposited sequentially on the heated substrates ($400K < T_S < 450K$).

During the deposition, a rotating substrate holder was successively positionned in front of the Cu evaporation source and in front of the Al evaporation source according to the sequence. The evaporation rates and film thicknesses were measured *in situ* by the vibrating quartz method, the quartz head being joined to the substrate holder. The number of layers for each constituent varied from six to ten in order to deposit Cu/Al/Cu ..Al/Cu structures The relative thicknesses of the layers were calculated to achieve the desired atomic ratio Cu/Al = 1.1. The thickness of the Cu layers was about 10 nm and its evaporation rate was 0 2 $\mathrm{nm\,s^{-1}}$, in the case of aluminium they were 13 nm and 0.2 $\mathrm{nm\,s^{-1}}$ respectively. A Cu excess is used because it has been shown, in the case of $CuInSe_2$, that such an excess improve the crystalline quality of the films [2]. After deposition the multilayer structures were introduced with a small amount of chalcogen in a Pyrex tube sealed under vacuum (10^{-4} Pa). Then the samples were annealed under chalcogen atmosphere. Chalcogens have a high vapour pressure, therefore during the annealing they were in the vapour state. The annealing temperature varied from 823 K to 853 K while the annealing time varied between 24 h and 48 h. The total thickness of the films after reaction with chalcogen was measured by a mechanical finger.

The films have been characterized by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and optical absorption.

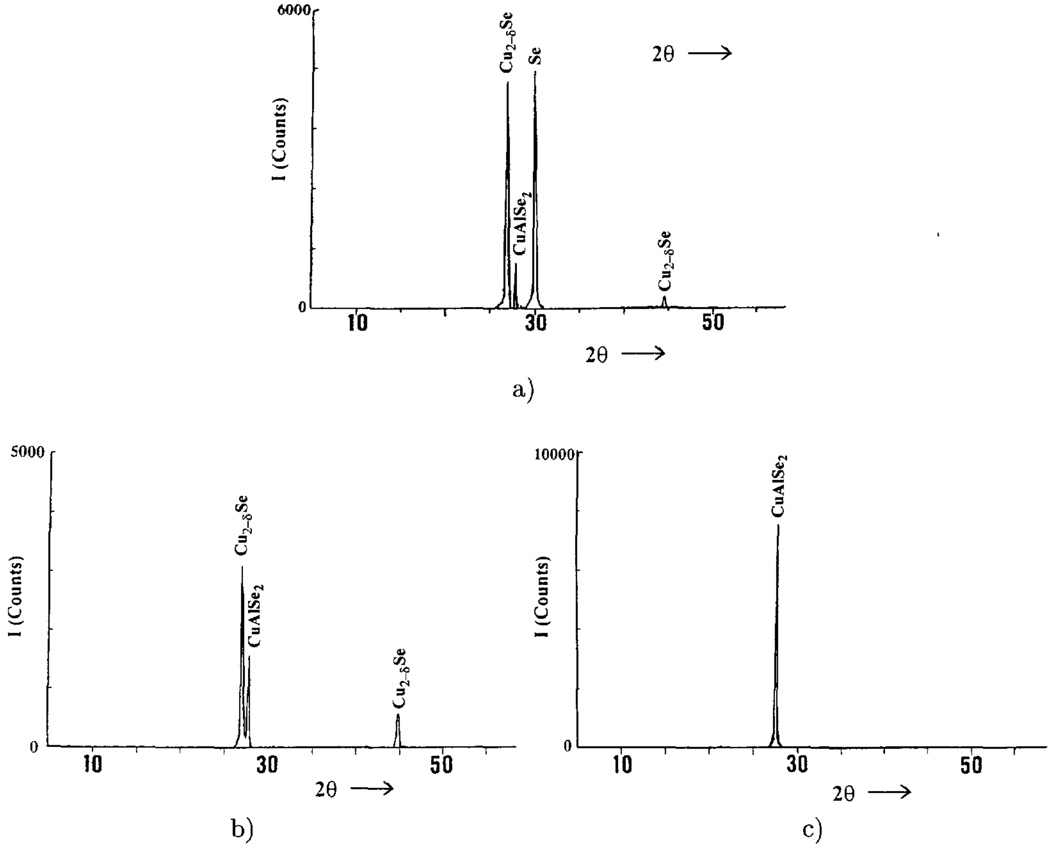
3. Experimental Results

The XRD of thin films on glass substrate are reported in Figure 1. It can be seen in Figure 1a that just after annealing, $CuAlSe_2$ but also $Cu_{2-\delta}Se$ and Se are present in the films The surface of these films appears to be quite inhomogeneous, small heaps and large grains of about 1 to 5 μm size appear, randomly distributed at the surface of the films (not shown).

It has been shown earlier that annealing under selenium atmosphere in a Pyrex tube induces some selenium condensation at the surface of the films during the cooling of the tube. This selenium excess at the surface of the films was sublimated by annealing the samples under dynamic vacuum for 6 h at 570 K After this annealing the Se peak has disappeared but those related to $Cu_{2-\delta}Se$ are still there (Fig. 1b) as the large grains residing on the surface. Therefore, as usually done in the case of $CuInSe_2$ [3], the binary compounds present in the powder have been etched in a 0.1M KCN solution for some minutes

The films were etched for periods of 1 min and XRD patterns were recorded after each treatment until the $Cu_{2-\delta}Se$ peaks disappear (Fig 1c). Then the visualization of the surface of the films shows that the large grains have disappeared. As shown by the X-ray diffraction spectrum (Fig. 1c), at the end of the process, only the (112) peak is clearly visible, which shows that the majority of the large crystallites are preferentially oriented along the (112) direction.

The samples have also been studied by XPS, however, quantitative information are difficult to obtain because the binding energies for Cu and Al are adjacent to each other (Cu3s and Al2s; Cu3p and Al2p; *etc.*). XPS lines are shown in Figure 2 for $CuAlSe_2$ thin films before and after KCN treatment.



a)

b)

c)

Fig 1. — XRD patterns of a multilayer Cu/Al/Cu. .Al/Cu thin film on a glass substrate a) after annealing under Se atmosphere. b) after 1st post-treatment (annealing under dynamic vacuum). c) after 2nd post-treatment (etching by a KCN solution)

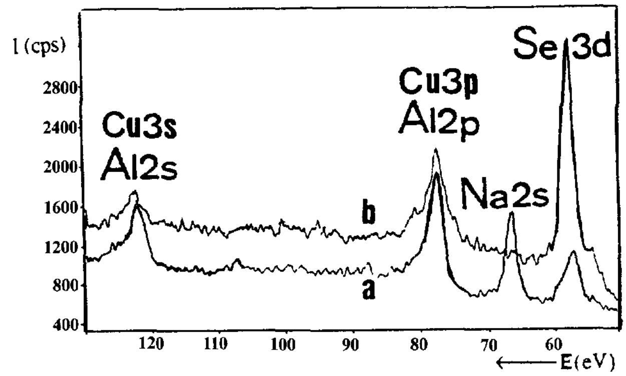


Fig 2. — XPS spectra of: a) CuAlSe$_2$ thin film on a glass substrate before KCN treatment, b) CuAlSe$_2$ thin films on a glass substrate *after KCN treatment.*

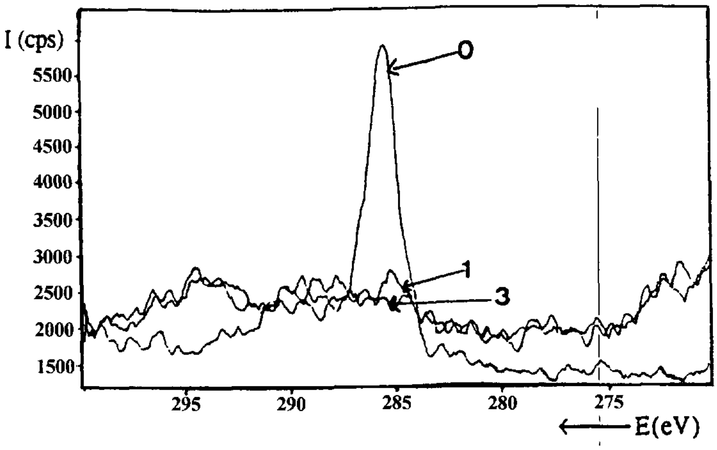


Fig 3 — XPS spectrum of the C1s peak after 0, 1, 3 minutes of etching.

For the discussion below the carbon peak of contamination at the surface of the samples has been taken as reference: C1s = 284.8 eV. The Se3d peak is situated at 55 eV while the binding energy of the $Cu2p_{5/2}$ is 932.3 eV. The Al peaks are adjacent to Cu peaks (Al2p and Cu3p; Al2s and Cu3s), therefore we have proceeded to a decomposition. The peak situated at 74.5 eV can be attributed to Al2p while the other situated at around 77 eV corresponds to Cu3p. The binding energy of the different elements Se3d, Al2p and $Cu2p_{5/2}$ are respectively 55.3 eV, 72.65 eV and 932.4 eV [4]. The electronegativity of Se being the highest of the three elements, its binding energy in the $CuAlSe_2$ compound should be smaller than that of the element alone, while that of the anions should be higher This is the case of the Al2p peak. In the case of $Cu2p_{5/2}$, it is well known that its binding energy is poorly sensitive to its oxidation state. Moreover, the binding energies obtained for Se and Cu are in good accordance with the values measured on other compounds of the same ternary chalcopyrite family such as $CuInSe_2$ [3].

The films have also been studied by XPS before KCN chemical etching. The result depends on the substrate. When a soda lime glass is used a new peak appears at 66 eV (Fig. 2a). In fact, simultaneously to this peak, another one situated at 1072 eV is also detected. This last peak has been already discussed in the case of $CuInSe_2$ [5]: it corresponds to Na diffusion from the soda lime substrate towards the surface of the films. Therefore the peak situated at 66 eV can be attributed to Na2s. The intensity of these Na peaks decreases when the etching time increases which shows that Na is accumulated mainly at the surface of the films. Fortunately Na is soluble in the KCN solution and the corresponding peaks disappear after chemical etching (Fig. 2b). The carbon contamination of the thin films has been controlled by the evolution of the C1s peak after etching (Fig. 3). It can be seen that this peak disappears after 1 or 2 min of etching. Therefore, we can conclude that there is no strong pollution in our thin films.

$CuAlSe_2$ is a direct gap semiconductor [1]. Therefore, the direct band gap can be deduced from the plot $(\alpha h\nu)^2$ *vs.* $h\nu$. The room temperature indicate a direct gap of 2.7 eV which is in accordance with the crystal [1].

The same process has been used to obtain $CuAlTe_2$. However in that case only large $CuAlTe_2$ grains embeded in a disordered "CuAl" matrix are obtained

4. Discussion, Conclusion

Oriented $CuAlSe_2$ thin films have been obtained by thermal annealing under selenium atmosphere of Cu/Al/Cu. Al/Cu thin sequentially deposited metallic layers. At the end of the process (annealing under selenium atmosphere, annealing under dynamic vacuum, chemical etching) the $CuAlSe_2$ films show properties expected. The optimum temperature for the annealing under selenium atmosphere appears to be around 820 K. The annealing duration is optimum at about 24 h. When the films are obtained on soda lime glass, there is Na at the surface of the films. The good crystallization and texturation of the films can be related to this Na diffusion, since it has been shown, in the case of $CuInSe_2$ [5], that the crystalline quality is strongly enhanced by Na diffusion through the films. This is corroborated by the fact that the $CuAlTe_2$ thin films obtained on Si substrates present the same XRD spectra than those obtained on glass substrate but with very small peaks intensity which is the consequence of a bad crystallization. So we have not studied these films more.

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