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On the influence of oxygen contamination on the properties of $CuAlX_2$ (X = Se, Te)

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$CuAlSe_2$ and $CuAlTe_2$ thin films have been obtained by annealing, in an open reactor, thin layers of the constituents deposited by evaporation in the stoichiometric ratio. It is shown that an annealing of half an hour at 673 K ($CuAlTe_2$) and 717 K ($CuAlSe_2$), under an argon flow, allows to achieve $CuAlTe_2$ and $CuAlSe_2$ chalcopyrite thin films. However, even after optimization of the technique, there is some oxygen contamination. It is shown that this contamination is not only related to Al but also to Te in the case of $CuAlTe_2$. This justifies the higher discrepancy between single crystal and $CuAlTe_2$ thin film performances. This is related to the contamination, not only of the grain boundary, which is the case of $CuAlSe_2$, but also of the crystallite induced by Te. On the other hand, structural and optical properties of $CuAlSe_2$ films are very similar to those measured on single crystals and epitaxial layers.

1. Introduction

Ternary I-III-VI_2 chalcopyrite semiconductors have received considerable attention in recent years because of their applications in photovoltaic devices, as shown by the use of $CuInSe_2$ (CIS) as absorbing films in solar cells [1]. Moreover some compounds of this family have larger gap than CIS ($Eg_{cis} = 1.01$ eV) and can be used for others applications such as buffer layer in solar cells but also electroluminescente semiconductor films in photo electroluminescente diodes (LED). $CuAlSe_2$ ($E_g = 2.67$ eV) and $CuAlTe_2$ ($E_g = 2.03$ eV) belong to these compounds [2]. We have earlier described a very simple and cheap technique which allows to obtain well crystallized $CuAlSe_2$ and $CuAlTe_2$ polycrystalline layers [3, 4].

However, finner analysis of the films, by using microprobe analysis, is necessary. It has been shown that the presence of oxygen in the films can be drastically decreased after optimization of the deposition and annealing conditions [5, 6]. Nevertheless, some oxygen is systematically present in the films at the end of the process: $4 < O$ at.% <10. This contamination is mainly related to the high affinity of aluminum to oxygen. However it is shown in the present paper that the oxygen interaction with the semiconductor films depends not only on aluminum but also on the chalcogen of the ternary compounds.

2. Experimental technique

The process used to obtain thin $CuAlX_2$ films has been described earlier [5, 6] and it will be recalled shortly here. The substrates were soda lime glass chemically cleaned and rinsed in deionised water. The depositions were done in a vacuum of 10^{-4} Pa. The substrate temperature during deposition was 300 K . Cu, Al, Se and Te of 99.999% purity were deposited in the sequence, earlier discussed [6], Al/Cu/Al/X/Al/Cu/...../X. The evaporation rate and the thickness were measured *in situ* by an hf quartz monitor. A rotating substrates holder allows to put alternatively the samples above the different crucibles. The layer thicknesses (10–45 nm) were calculated to achieve a near stoichiometric composition.

The $CuAlX_2$ films were then synthesized by annealing under an argon flow. We have shown in earlier papers [5, 6] that the optimum annealing time is half an hour. Therefore all the films studied in the present work have been annealed for half an hour.

At the end of the synthesis the samples were stored in a plastic box at room atmosphere.

Using X-ray diffraction, the films were analysed in order to investigate the compound and/or phase formation and to estimate the grain size as well as their preferential orientation. X-ray diffraction measurements were carried out on an automated step-scanned Siemens diffractometer with Cu Kα radiation source ($\lambda = 0.15406$ nm). The d_{hkl} spacings were given directly by the graphics program EVA used by the diffractometer.

For microprobe analysis, we used a JEOL 5800 microscope and a built-in software program (PGT-IMIX PTS) that did the background correction and gave the percentage of the elements (down to C), which allows to obtain quantitative analysis of the relative atomic percentage of the oxygen present in the films.

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X-ray photoelectron spectroscopy measurements were performed with a magnesium X-ray source (1253 eV) operating at 10 kV and 10 mA. The XPS study was made at the University of Nantes-CNRS and a Leybold (HS 12 model) spectrometer was used.

The transmission measurements were carried out at room temperature using a Carry spectrophotometer. The measurements were carried out at wavelengths from 2 μm to 0.4 μm. The Optical studies were performed at the LPC-IMN.

3. Experimental results

The microprobe analysis showed that the films could be strongly contaminated by oxygen (up to 40 at. %) during the deposition process. Therefore, while the deposition rate of aluminium has been increased from 0.2 nm/min to 1 nm/min, the deposited aluminium films were immediately covered with a chalcogene layer in order to prevent oxide formation. By using such a process, the relative atomic concentration of oxygen present in the films at the end of the deposition was decreased to 10 at. % or less, whatever the chalcogene is.

The thickness of the films ranged from 200 nm to 750 nm, in that range the thickness variation did not significantly affect the experimental results.

It has been shown [7, 8] that often during Cu-III-VI_2 thin films growth some $Cu_{2-x}VI_x$ forms at the surface of the films. Systematically this upper layer is removed by KCN etching [1]. KCN is very useful for such etching because CN-complex very easily with noble metals such as Au, Ag and Cu... which allows the chemical etching of the copper binary compounds. Therefore the results described here concern films after KCN treatment [5, 6].

As shown Fig. 1, after annealing half an hour under argon flow at 673 K ($CuAlTe_2$) [5] or 773 K ($CuAlSe_2$) [6], the films are crystallized in the expected chalcopyrite structure as demonstrated by the presence of the (101) and (103) peaks; which excludes the disordered sphalerite structure. The temperatures used have been found to be the optimum values to obtain well crystallized films with small oxygen contamination. The experimental results obtained by XRD measurements are summarized Table I. As usual in such I-III-VI_2 compounds the peak corresponding to the (112) direction is dominating. Also are reported in this table, the lattice parameters calculated from the inter planar spacing measured by XRD. It can be seen that there is a good agreement between the measured values and those obtained with a single crystal.

However some small difference should be noted mainly in the case of $CuAlTe_2$ since the experimental incertitude related to the use of glass substrate, which thickness can vary slightly from one sample to another one, can be estimated to ±0,001 nm.

EPMA results are summarized in Table II. It can be seen that the small oxygen contamination ($4 < O$ at. % <10) is systematically associated with a small aluminum excess in comparison with copper ($Al/Cu > 1$). Moreover it appears that the oxygen contamination is slightly higher in $CuAlTe_2$ films.

TABLE I Lattice parameters

	$CuAlSe_2$			$CuAlTe_2$		
Sample	JCPDS 44-1269	Thin film	Δ (nm)	JCPDS 75-0102	Thin film	Δ (nm)
a (nm)	0.560	0.561	+0.001	0.596	0.604	+0.008
c (nm)	1.097	1.098	+0.001	1.197	1.195	−0.002

TABLE II Average quantitative EPMA analysis ($*$: X = Se or Te)

	Atomic percentage			
	Cu	Al	X*	O
theoretical	25	25	50	0
$CuAlSe_2$	24 ± 2	27 ± 2	44 ± 2	5 ± 2
$CuAlTe_2$	21 ± 2	24 ± 2	45 ± 2	10 ± 2

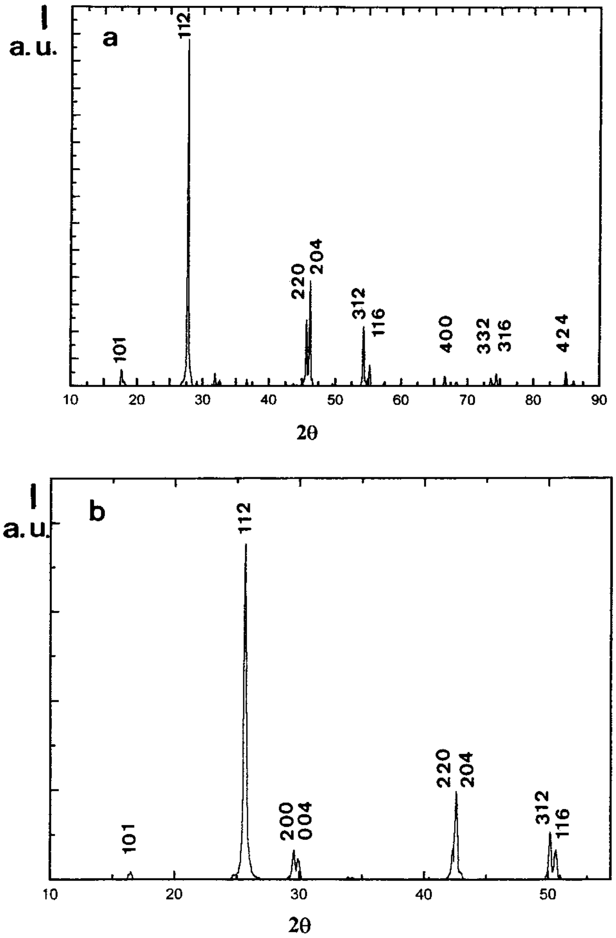


Figure 1 X-ray diffractogramms of a: (a) $CuAlTe_2$ film after annealing half an hour at 673 K. (b) $CuAlSe_2$ film after annealing half an hour at 773 K.

XPS analyses of the films have been discussed in previous papers [4, 5]. In the present work, we have focused our investigation more precisely on the chalcogen behavior after contact with oxygen and the consequences on the under layer.

First, thin pure selenium and tellurium films have been investigated. It can be seen on Fig. 2a, b that the selenium is not chemically contaminated by oxygen even at the surface (Se3d = 55.3 eV in pure Se and 59.2 eV in SeO_2). At the contrary, there is some systematical interaction between the tellurium and the oxygen with some TeO_2 formation ($Te3d_{5/2} = 583.0$ eV in pure Te and 586.5 eV in TeO_2) (Fig. 3a, b). The same result is obtained when the sequentially deposited structures (Cu/Al/X/Al/Cu . . . Al/X with X = Se or Te) are submitted to air atmosphere before annealing. Moreover, after annealing, XPS analyses of the ternary thin films show that if in the $CuAlSe_2$ films, Se is not contaminated by oxygen, tellurium at the surface is oxidized in the case of $CuAlTe_2$ (Figs 2c, d and 3c, d).

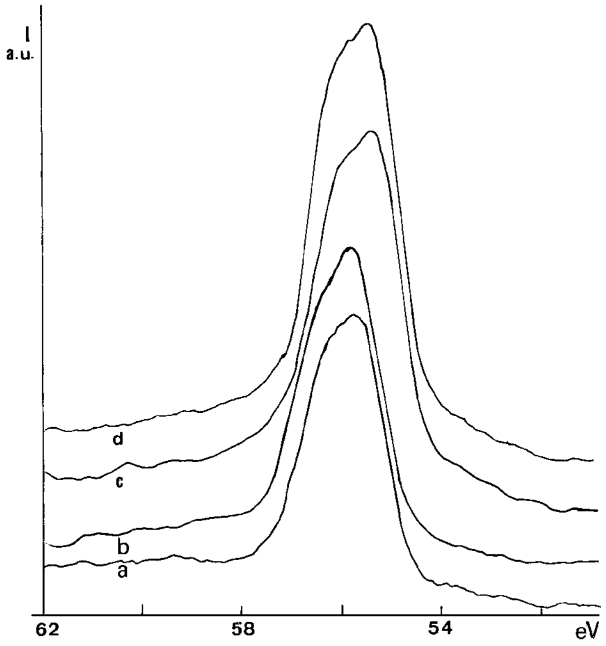


Figure 2 XPS spectrum of the Se3d peak: (a) pure selenium film before etching (b) pure selenium film after one minute of etching. (c) in a $CuAlSe_2$ film before etching. (d) in a $CuAlSe_2$ film after one minute of etching.

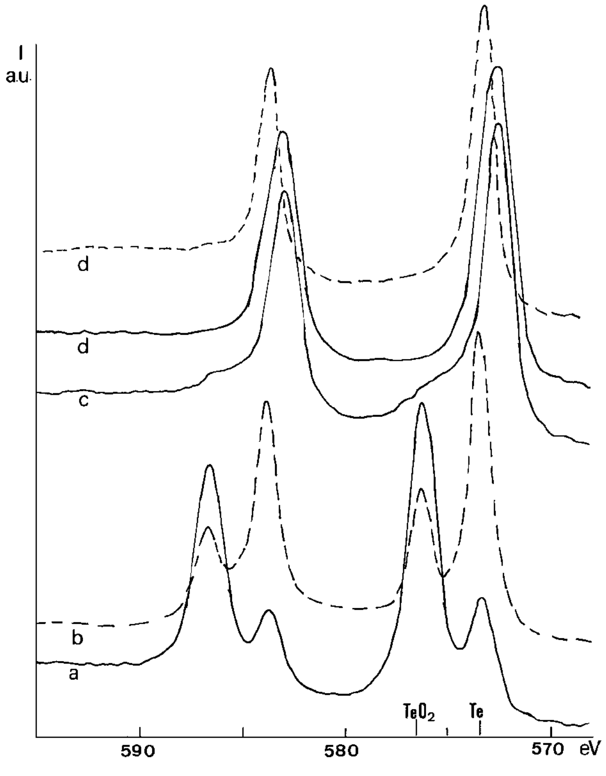


Figure 3 XPS spectrum of the Te3d peak: (a) pure tellurium film before etching (b) pure tellurium film after one minute of etching. (c) in a $CuAlTe_2$ film before etching. (d) in a $CuAlTe_2$ film after one minute of etching. (e) at the interface Se/Te after selenium etching.

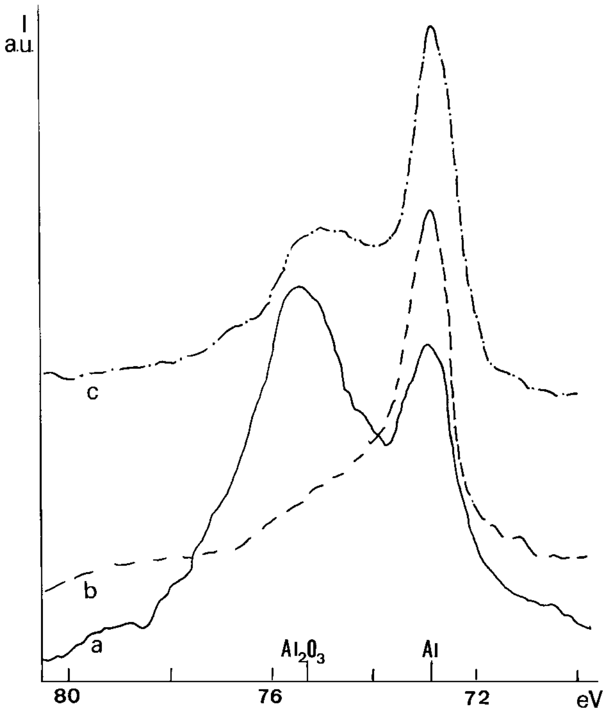


Figure 4 XPS spectra of Al at the interface (when the Al2p line appears after chalcogen etching): (a) in Al/Te structure after air exposure. (b) in Al/Se structure after air exposure. (a) aluminum at the interface Te/Al after selenium and tellurium etching.

Therefore, we have proceeded to some more careful investigation on the oxygen influence on the different structures. When aluminum and tellurium layers are sequentially deposited, after air exposure there is not only oxidation of the surface of the Te film but also quick formation of a continuous aluminum oxide film at the Al/Te interface (Fig. 4a). When aluminum and selenium are sequentially deposited, not only the selenium surface is not oxidized but also the aluminum film is preserved from large oxidation (Fig. 4b). When these Al/Te layers are covered by a Se film before air exposure, there is not any oxidation not only of the Se capping layer but also of the tellurium (Fig. 3e), while the small aluminum oxidation is similar to that obtained in the case of Al/Se structure (Fig. 4c), it corresponds to aluminum oxidation during the deposition process [9]. When the crystalline structure of the Se and Te films is checked by XRD, it can be seen that selenium films are amorphous while those of tellurium are polycrystalline but continuous has shown Fig. 5.

Moreover, after etching of the $CuAlX_2$ (X = Te, Se) films the binding energy of the O1s peak of the oxygen still present in the films is about 532.5 eV whatever the chalcogen, which cannot be attributed to copper oxide, but corresponds to some aluminum oxide [10].

The absorption coefficient α has been calculated from the measured transmission T ($\log \frac{1}{T} = \mathrm{OD}$ (optical density: OD)) of two samples with different

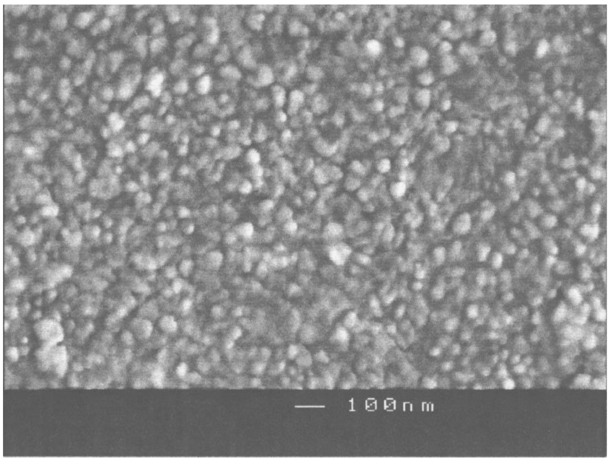


Figure 5 Surface visualization of a thin Te layer deposited in a stacked elemental layer structure before annealing.

thicknesses:

$$\alpha = \frac{1}{t_2 - t_1} \log\left(\frac{T_1}{T_2}\right)$$

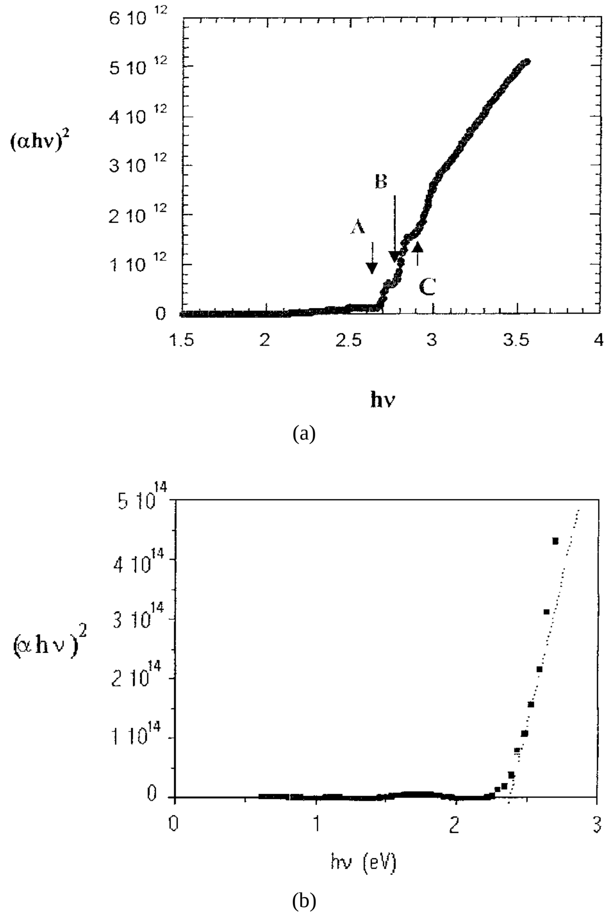
with t the thickness of the film.

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.

$CuAlSe_2$ and $CuAlTe_2$ being direct band gap semiconductors, the plots of $(\alpha h\nu)^2$ versus the photon energy hν are reported Fig. 6 and Table III, since, for allowed direct band gap transition, the absorption α can be related to the photon energy by:

$$(\alpha h\nu)^2 = A(h\nu - Eg)$$

where A is a constant and Eg is the optical energy gap.



(a)

(b)

Figure 6 Plots of $(\alpha h\nu)^2$ versus the photon energy hν for: (a) $CuAlSe_2$ film, (b) $CuAlTe_2$ film.

TABLE III Optical transition

Optical transition (eV)		A	B	C
$CuAlSe_2$	Single crystal [9]	2.65	2.86	3.01
	Thin film	2.66	2.78	2.91
$CuAlTe_2$	Single crystal [2]	2.06		
	Thin film	2.3		

The band gap can be extrapolated from the intercept of the straight line issued from the high absorption domain and the photoenergy axis. It can be seen that if the properties of the $CuAlSe_2$ films are very similar to that of references [2], there is some discrepancy in the case of $CuAlTe_2$. The absorption spectrum of the $CuAlTe_2$ films is not so well discriminated and only the band gap can be estimated.

4. Discussion

As proposed, the discussion will be focused on the influence of oxygen on the two ternary compounds presently studied. A more general description of the structural, optical and electrical behavior of the compounds has been given elsewhere [3–6].

First it should be noted that the oxygen contamination in $CuAlTe_2$ (7–10 at.%) is significantly higher than in $CuAlSe_2$ (4–7 at.%). Moreover it is shown from XRD measurements that if the chalcopyrite structure expected is systematically obtained, there is some small differences between the lattice parameters of single crystals and those measured here. Remarkable variations are obtained only in the case of the $CuAlTe_2$. There is a small increase of the a parameter while the c axis decreases slightly. At the same time, the optical properties of $CuAlSe_2$ films are more similar to that of the corresponding single crystal than in the case of $CuAlTe_2$ samples.

Therefore, it appears that if aluminum is the main cause of oxygen contamination, the nature of the chalcogen is not neutral. This is in good agreement with the different reactivity with oxygen of the chalcogen as shown by XPS.

The presence of some Al_2O_3 in the films in the deposited condition used presently is very probable as shown by the presence of a residual peak on the high binding energy domain of the Al2p XPS spectra whatever the sample studied is (Figs 3b, 4b). This partial oxidation can be predicted from the work of Kim and co-cookers [8]. However a careful observation of the XRD diagram neither indicate the presence of polycrystalline alumina nor of an amorphous phase (no broad diffusion domain visible in the 2θ domain: 10°–30°). Therefore Al_2O_3 should be present in the films in very small domains, there is probably some segregation of this oxide at the grain boundaries. It can be thought that this amorphous AlO_x, segregated at the grain boundary, is present in both compounds. It corresponds to the unavoidable oxygen present in the films (4 ± 1 at.%). By comparison with $CuAlSe_2$ oxygen contamination, the small excess present in the $CuAlTe_2$ films (3–5 at.%) will interact with the ternary compound itself, mainly with the Al as shown by XPS. This justifies not only the small excess of aluminum detected in the films, which corresponds to this oxide formation, but also the good properties of $CuAlSe_2$ compared to those of $CuAlTe_2$.

Therefore $CuAlSe_2$ films are composed of nearly pure ternary crystallites crystallized in the chalcopyrite structure with some AlO_x dispersed at the grain boundaries. These crystallites have properties (structure, optical transitions...) which are not modified by the oxygen and therefore similar to those of $CuAlSe_2$ single crystals [11].

On the contrary the 3–5 at.% more of oxygen present in the $CuAlTe_2$ films enter the crystallites themselves which justify the modification of their properties.

The lattice parameters are sensibly different from those expected. There is an increase of the a parameter and a small decrease of c.

The oxygen present in the crystallites can be substituted to tellurium and/or intercalated in the crystallites.

The atomic radius of oxygen is smaller than that of tellurium, which could justify, for geometrical reason, the decrease of the lattice parameters. However its electronegativity is higher, which could justify, for electrostatic reason, an increase of the a lattice parameter, because this includes an increasing repulsion between atoms that are negatively charged [12, 13], which could justifies the increase of a. Moreover intercalation could also induces an increase of the lattice parameters. However c decreases slightly and more probably oxygen is substituted to tellurium which is in good agreement with the composition analysis, since there is some chalcogen deficiency.

We have shown by XPS that, not only tellurium is spontaneously reactive with oxygen while selenium is not, but also that oxygen diffuses spontaneously through the overall polycrystalline tellurium layer, while it does not through the amorphous selenium layer. Therefore not only aluminum reacts partly with the residual oxygen, but also, even in smaller proportion, with tellurium but not with selenium. During the annealing, if oxygen bonded to aluminum will give mainly Al_2O_3, the oxygen bonded to tellurium will interact with the atomic environment which will induce the growth of crystallites of ternary compounds contaminated with O_2 as described above.

The higher contamination of tellurium compounds can be, at least partly, understood with the help of the electronegativity (χ) difference between Se and Te. $\chi_{\text{Se}} = 2.5$ while $\chi_{\text{Te=}} = 2.1$, therefore the interaction with oxygen, ($\chi_{\text{o}} = 3.5$), is higher in the case of Te. Moreover the bond stability between any metal and chalcogen, which is related to the electronegativity difference χ_{M}-$\chi_{\text{chalcogen}}$ is higher in the case of selenium. We have already discussed this electronegativity influence on the chalcogen compound stability [14]. The stability of these compounds increases with the electronegativity difference between the chalcogen and the metal. Therefore the selenium compounds are more stable than the tellurium compounds, often the former are stoichiometrics, while the later are tellurium deficient which facilitates oxygen contamination [15]. This contamination, in the present work, not only induces lattice parameters variation but also introduces some disorder in the films, which explains the discrepancy between the band gap measured and that expected.

5. Conclusion

The ternary compounds $CuAlSe_2$ can be obtained in the expected chalcopyrite structure by using the cheap and simple technique of annealing in open reactor.

However if oxygen contamination can be drastically decreased by using optimized technique there is systematically some residual oxygen present in the films at the end of the process. The oxygen contamination is slightly higher in the case of $CuAlTe_2$ films. This fact could be correlated to the structural and optical properties of the films, they are more similar to those of the corresponding single crystal in the case of $CuAlSe_2$.

Probably in that case the oxygen precipitates with the aluminum excess at the grain boundary of the films which allows to obtain crystallite with properties nearly similar to those of $CuAlSe_2$ single crystal. In the case of $CuAlTe_2$ oxygen reacts in addition with some tellurium as shown by XPS which allows oxygen to enter the crystallites and modify theirs properties. This result is confirmed with the help of electronegativity difference between Se and Te.

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