Growth and physicochemical characterization of CuAlTe$_2$ films obtained by reaction, induced by annealing, between Cu/Al/Te/Al/Cu ... Al/Cu/Al/Te layers sequentially deposited

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CuAlTe$_2$ thin films have been synthesized by annealing under an argon flow a multilayer structure of thin Cu, Al and Te layers sequentially deposited by evaporation under vacuum. The films have been characterized by X-ray diffraction, microprobe analysis, photoelectron spectroscopy and Raman scattering. At the end of the process, the XRD spectra demonstrate that textured CuAlTe$_2$ films have been obtained with preferential orientation of the crystallites along the (112) direction. The Raman patterns are in good accordance with the reference. The XPS spectra show that the binding energies of the elements are in good agreement with bonds of CuAlTe$_2$. Even after a decrease of the oxygen contamination by improvement of the depositing process the oxygen present in the films is found to be about 12 at %. © *1999 Kluwer Academic Publishers*

1. Introduction

The need for inexpensive efficient solar cells forces the exploration of new semiconductors in thin film form. Ternary I-III-VI$_2$ chalcopyrite semiconductors is a very large family. The CuInSe$_2$ and its derivatives have been extensively investigated in the last ten years because of their large potential application in the photovoltaic domain [1–5]. However some other chalcopyrite compounds such as CuAlX$_2$ (X = S, Se, Te) have not been sufficiently investigated. Few works on CuAlSe$_2$ and CuAlS$_2$ are available [6, 7] and to our knowledge only one group has studied CuAlTe$_2$ [8, 9]. It has been shown that CuAlTe$_2$ films can be obtained by R.F sputtering. In this work we will show that, after sequential deposition of Cu, Al and Te layers, CuAlTe$_2$ films are obtained by annealing in argon flow. Our elaboration uses the widely accepted technique of annealing in flowing argon to obtain homogeneous and textured thin films of different compounds [10].

2. Experimental
2.1. Films preparation

The substrates were polished soda lime glass, chemically cleaned. The Cu, Al and Te layers were sequentially deposited in vacuum (base pressure 5 10^{-4} Pa) by thermal evaporation from three tungsten crucibles.

The CuAlTe$_2$ films were synthesized by reaction between the constituants, induced by annealing (1/2 h at 620 K ≤ T ≤ 820 K), in an argon flow into an oven. Layers of Cu, Al and Te were deposited sequentially on substrates. During the deposition a rotating substrate holder was successively positionned in front of the Cu evaporation source, in front of the Al evaporation source and in front of the Te evaporation source according to the sequence Cu/Al/Te/Al/Cu/Al/Te ... Al/Cu/Al/Te. The evaporation rates and layer thicknesses were measured *in-situ* by the vibrating quartz method, the quartz head being joined to the substrate holder. The number of layers for Cu and Te constituents varied from six to ten, twelve to twenty for Al, in order to deposit the desired multilayer structures. The relative thicknesses of the metallic layers were calculated to achieve the desired atomic ratio Cu/Al = 1.1 since it has been shown that a small Cu excess improve strongly the crystallization of the ternary chalcopyrite compounds. After deposition the multilayer structures were introduced in an oven for an annealing with an argon flow (30 l/h). The annealing time was half of an hour and the temperature varied from 620 to 820 K. The thickness of the Cu layers was about 10 nm and the evaporation rate was 0.2 nm/s, in the case of Al layers they were 14 nm and 1 to 2 nm/s respectively and in the case of Te layers they were 60 nm and 1 to 2 nm/s respectively. The

total thickness of the films after annealing was measured by a mechanical finger and varied from 300 to 400 nm.

The purity of Al was 99.99, while that of Cu and Te was 99.999. The argon used during the process has purity (in at%) of 99.999%. The impurity level was: $H_2O = 3$ ppm, $O_2 = 3$ ppm, $N_2 = 10$ ppm.

2.2. Characterization techniques

The films have been physicochemically characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), microprobe analysis (EPMA) and Raman diffusion.

An X-ray diffractometer, using monochromatic CuK_α radiation, was employed to obtain the diffraction
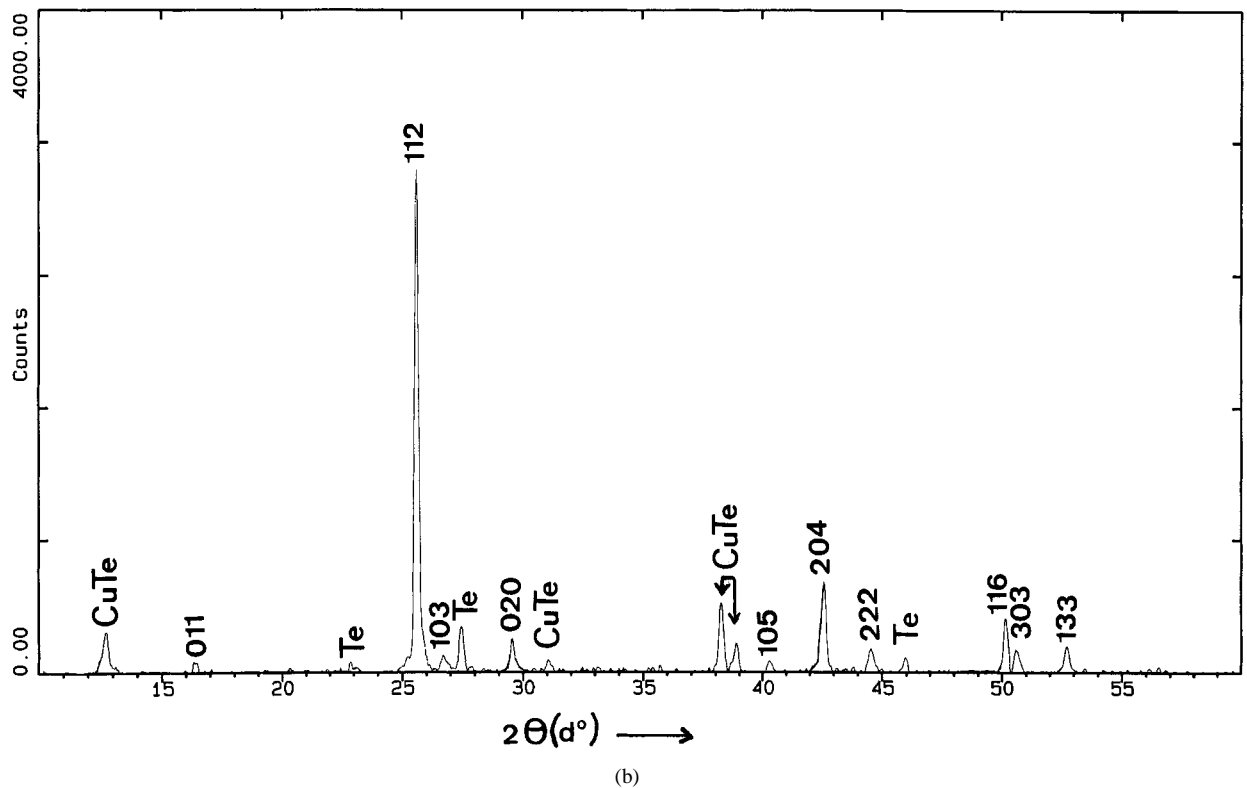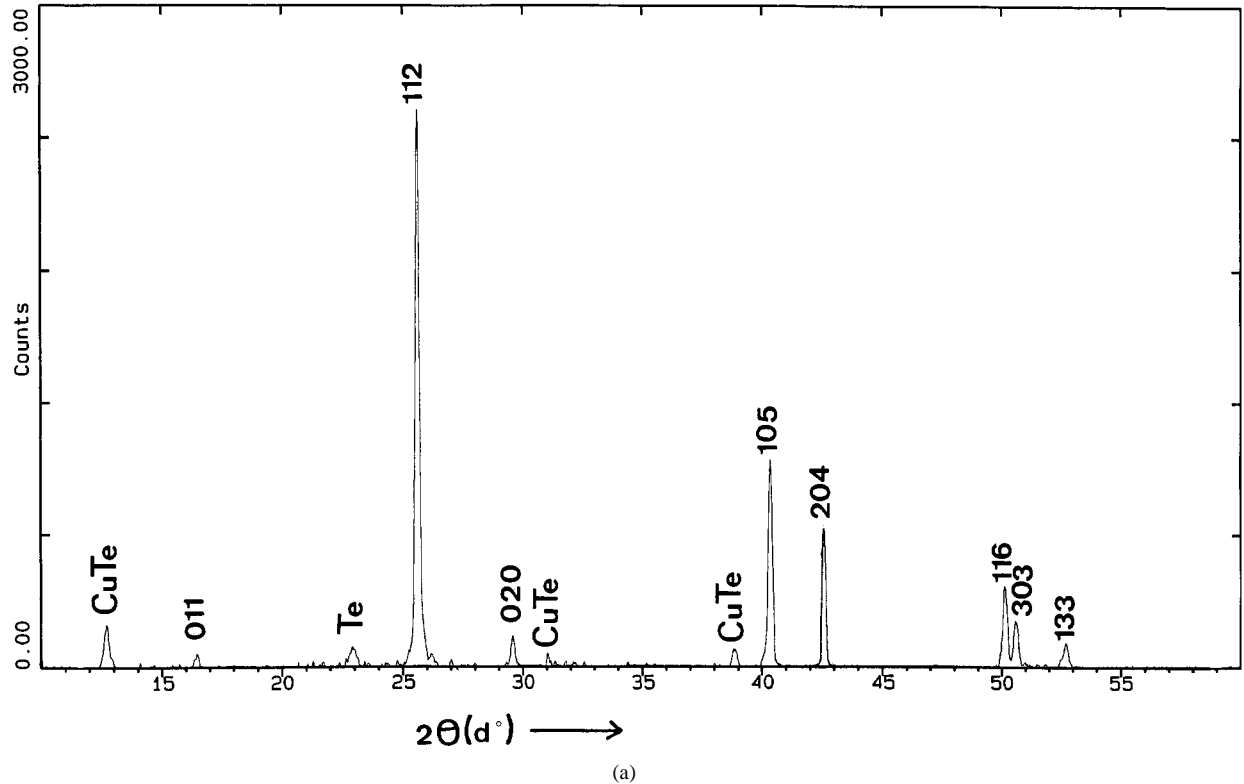

Figure 1 XRD patterns of CuAlTe$_2$ films: (a) multilayer Cu/Al/Te/Al/Cu/Al/Te . . . Al/Cu/Al/Te structure annealed at 620 K for 1/2 h under an argon flow, (b) multilayer Cu/Al/Te/Al/Cu/Al/Te . . . Al/Cu/Al/Te structure annealed at 670 K for 1/2 h under an argon flow, and (c) multilayer Cu/Al/Te/Al/Cu/Al/Te . . . Al/Cu/Al/Te structure annealed at 820 K for 1/2 h under an argon flow. (*Continued*).
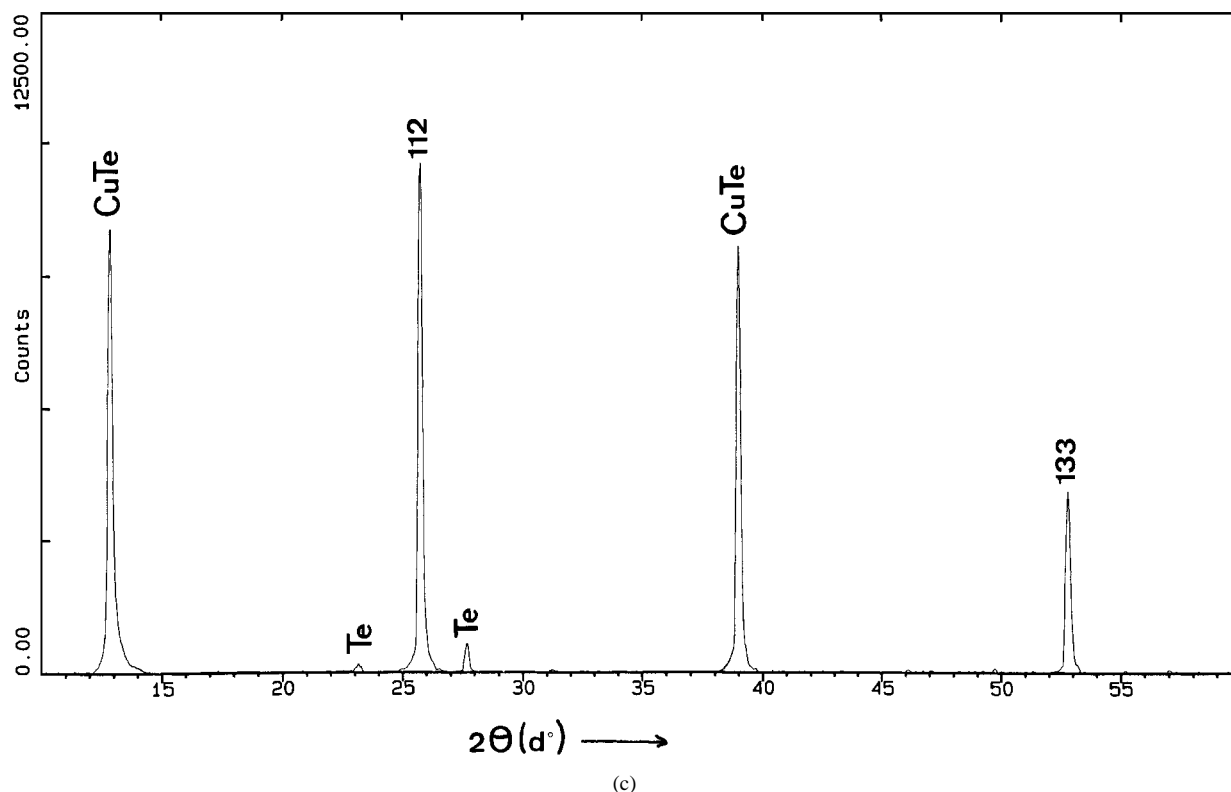
Figure 1 *(Continued)*.

(c)

patterns of the films. The FWHM was given directly by graphics program EVA used by the diffractometer (SIEMENS D5000).

XPS analysis was carried out at the University of Nantes (CNRS) on a Leybold HS-12 spectrometer. XPS measurements were performed with a magnesium X-ray source (1253 eV) operating at 10 kV and 10 mA. Data acquisition and treatment were realized through a computer and a standard program. At the surface of the films there is a carbon-carbon (C–C) bond corresponding to surface contamination. In the apparatus used this C–C bond had a well defined position at 284.8 eV. This carbon peak was used as reference to estimate the electrical charge as the films were deposited on glass. Contamination in depth of the films was checked by recording successive XPS spectra obtained after argon ion etching for shorts periods. Sputtering was accomplished at pressures of less then 5×10^{-4} Pa, a 10 mA emission current and a 3 kV beam energy using an ion gun. With these experimental conditions all the surface of the samples was sputtered.

An electron microscope, equipped with a microprobe analyser, was used to check the composition of the films.

Raman spectra were measured at room temperature using a BRUKER model RFS 100. The samples were excited by a Nd:YAG laser with a wavelength of 1064 nm. The laser power and the scale number necessary to obtain good signal noise ratio were 100 mW and 500 respectively.

3. Experimental results and discussion
3.1. Preliminary
In a previous work [7] we have shown that highly oriented $CuAlSe_2$ thin films can be obtained by the thermal annealing under selenium atmosphere of Cu/Al/Cu . . . Cu/Al thin metallic layers sequentially deposited. At the end of the process (annealing under selenium atmosphere (820 K, 24 h), annealing under dynamic vacuum (570 K, 6 h), chemical etching) the $CuAlSe_2$ films show properties close to those of a $CuAlSe_2$ reference powder. The chemical etching with a KCN solution (0.1 M) was necessary to eliminate the binary phases $Cu_{2-x}Se_x$ still present in the films after the two annealings.

If we use this technique to growth $CuAlTe_2$ films (multilayer Cu/Al/Cu . . . Al/Cu structure annealed under Te pressure) we obtain, as in the case of $CuAlSe_2$, an XRD signal which can be partly attributed to $CuAlTe_2$. However it appears that it corresponds to $CuAlTe_2$ crystals randomly distributed in a binary matrix. Moreover the oxydation of the films is strong. So we try to avoid the formation of these foreign phases by changing the process. First we use a multilayer Cu/Al/Te/Al/Cu/Al/Te . . . Al/Cu/Al/Te structure. This structure avoids the reaction between Cu and Te at the beginning of the annealing which limits the spontaneous formation of binary phases $Cu_{2-x}Te_x$ as we will show with the results described below. Then this structure is put in an oven with an argon flow for an annealing of 1/2 h.

3.2. XRD and micropobe results
XRD spectra of $CuAlTe_2$ films at the end of the process are shown in Fig. 1 for different annealing temperatures. It can be seen that for annealing temperature of 620 K (Fig. 1a) and 670 K (Fig. 1b) the XRD spectra are nearly the sames. For 620 K (Fig. 1a) two small Te peaks appear with a very small CuTe peak. The (112) peak is strong compared to the others. For 670 K

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(Fig. 1b) the small Te peaks have disappeared and the CuTe peaks are a little bit stronger. The (112) peak and its relative intensity are more strong than for 620 K which demonstrates a better crystallisation and orientation of the crystallites along the (112) direction. For an annealing temperature of 820 K (Fig. 1c), the (112) peak is very strong but binary CuTe peaks are also very strong which demonstrates that a higher annealing temperature induce binary CuTe formation in the films. It should be noted that the FWHM of the peaks being too small, it is not possible to calculate the grain size. We can only say that the crystallites are larger than 200 nm [12].

The results of micropobe analysis are given in Table I.

It can be seen in Table I that the films are stoichiometric (at % Te/at % Cu $\approx$ 2) for an annealing temperature of 670 K but with a non trivial concentration of oxygen

TABLE I Atomic concentration for different annealing temperatures

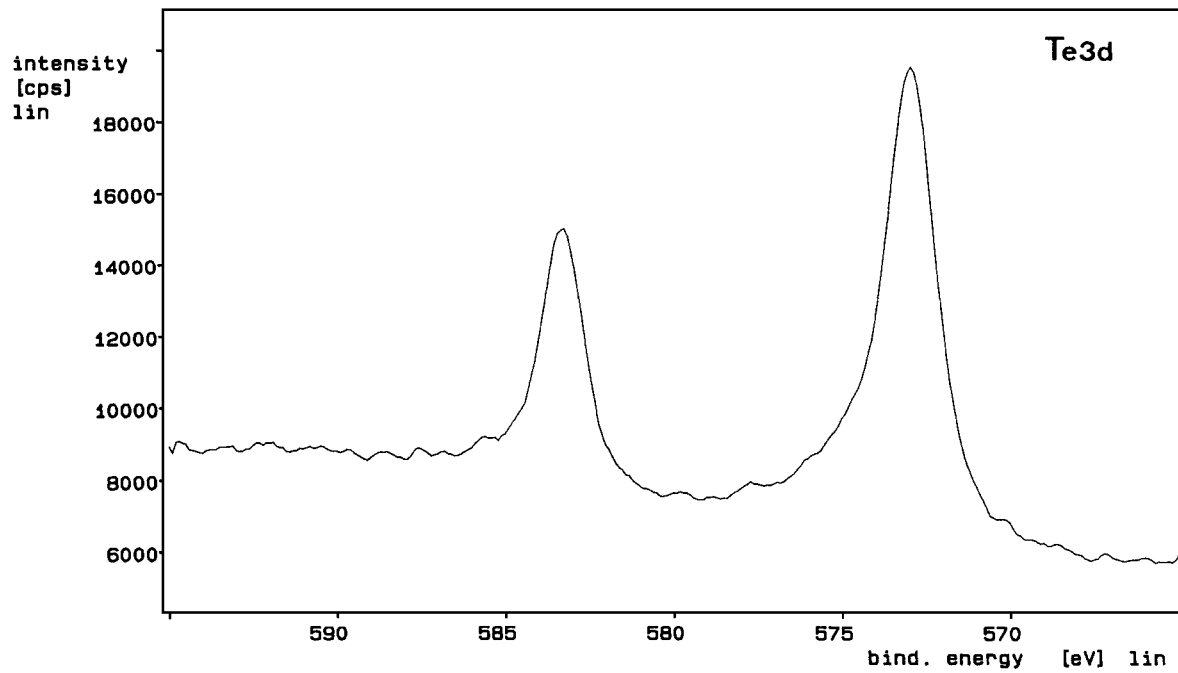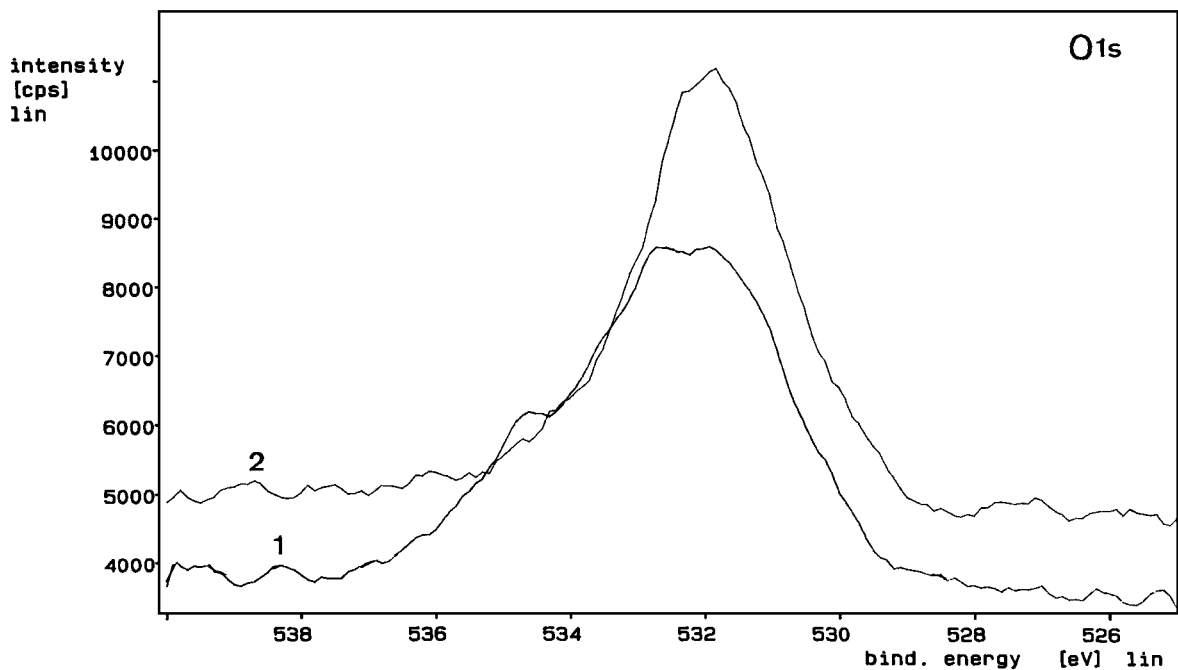| Annealing temperature (K)	Atomic concentration (%)			
	Cu	Al	Te	O
620	13	18	57	12
670	20	27	41	12
820	10	23	35	32
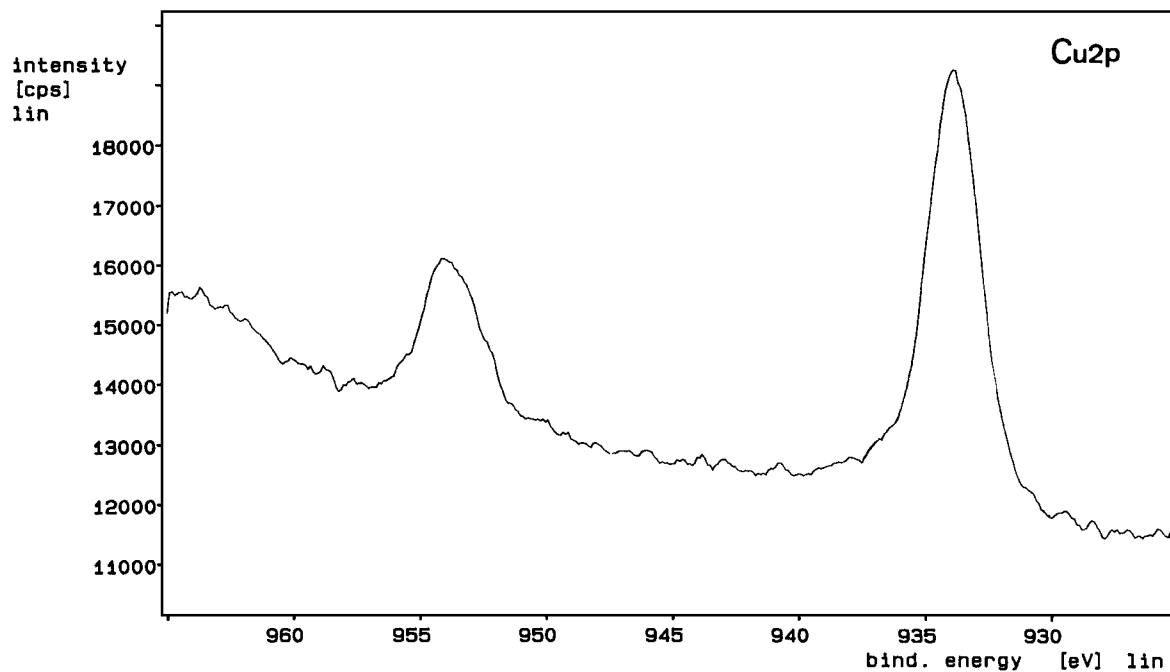
(a)
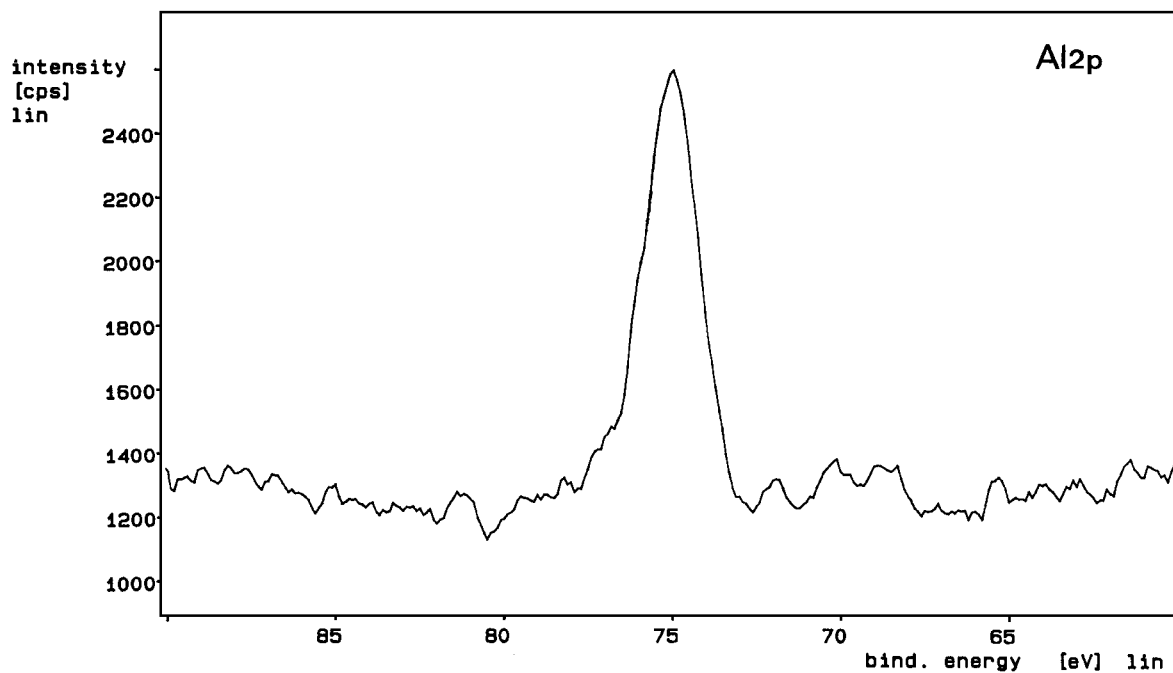
(b)

Figure 2 XPS spectra of a CuAlTe$_2$ film obtained at 670 K after an etching of 3 min: (a) Cu2p, (b) Al2p, (c) Te3d, and (d) O1s (1, no etching; 2, 3 min etching). (*Continued*).

intensity [cps] lin

Te3d

18000
16000
14000
12000
10000
8000
6000

590   585   580   575   570

bind. energy   [eV] lin

(c)

intensity [cps] lin

O1s

10000
9000
8000
7000
6000
5000
4000

2

1

538   536   534   532   530   528   526

bind. energy   [eV] lin

(d)

Figure 2 (Continued).

(12%). This concentration of oxygen explain the Al excess due to Al_2O_3 present in the films. For 620 K, the oxygen concentration is the same but there is a strong Te excess: this is due to Te which has not reacted with Cu and Al metallic layers due to an annealing temperature too small. For 820 K, there is a strong deficit of Te and a strong concentration in oxygen (32%): this is due to the annealing temperature which induce the Te substitution by oxygen to make up Al_2O_3. The Te release involve a reaction with Cu to make up CuTe. Kim *et al.* [9] show that an oxidized layer is formed at start of the Al deposition and that a less extensively oxidized Al layer is deposited if the deposition rate is fast. So the evaporation rate of Al, during the deposi-

tion of the multilayer structure, was faster as possible and the time between two layer depositions was shorter as possible to avoid the Al oxidation during deposition. We can conclude from this study that 670 K is the best annealing temperature.

3.3. XPS characterization

It has been shown by the XRD and micropobe analysis study that $CuAlTe_2$ films crystallized in the chalcopyrite structure can be obtained. The chemical state of these films have been studied by X-ray photoelectron spectroscopy and Raman scattering.

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By XPS analysis, 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.). Moreover the binding energy and the sensibility factors of $Cu2p_{5/2}$, Al2p and Te3d peaks, which are usually used for quantitative analysis, are very different, which induce uncertainties. XPS lines are shown in Fig. 2 for a $CuAlTe_2$ thin film obtained at 670 K.

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 Te3d doublet is situated at about 580 eV while the binding energy of the $Cu2p_{5/2}$ is 932.3 eV. Al and Cu being adjacent (Fig. 2b) we have proceeded to a decomposition of the peak. It can be seen on the Fig. 3 that the peak situated at 74.5 eV can be attributed to Al while the other situated at about 77 eV corresponds to Cu. The pollution of the films has been controlled by the evolution of the carbon and oxygen peaks after etching.
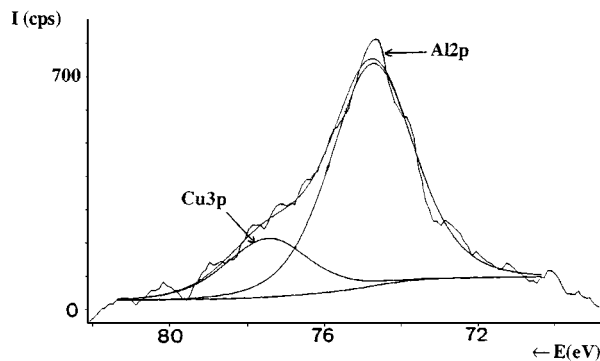
The carbon peak disappear after 1 or 2 min of etching (not shown). It can be seen in Fig. 2d that the oxygen peak is nearly the same even after 3 mn of etching. We can conclude that the oxygen concentration is constant in the bulk while the carbon is a surface contamination.

3.4. Raman diffusion

The chemical state of the films has been also checked by Raman diffusion in order to confirm the $CuAlTe_2$ occurence. The results obtained are presented in Fig. 4. The main peaks obtained are situated at 123 and 141 cm^{-1} which is in good accordance with the results that we have obtained for $CuAlSe_2$ [5]. The slope of the spectrum is similar to that of the $CuAlSe_2$ spectrum with a shift, towards smaller wavenumber, which is expected since the atomic weight of Te is higher than that of Se.

4. Conclusion

$CuAlTe_2$ films, crystallized in the chalcopyrite structure with the crystallites oriented along the (112) direction, are obtained by annealing a multilayer Cu, Al, Te structure under an argon flow at 670 K for 1/2 h. The Raman peaks obtained for the thin films are in good agreement with these of the references. The optimum temperature for the annealing is found to be 670 K. However there is 12 at % of oxygen in the films.

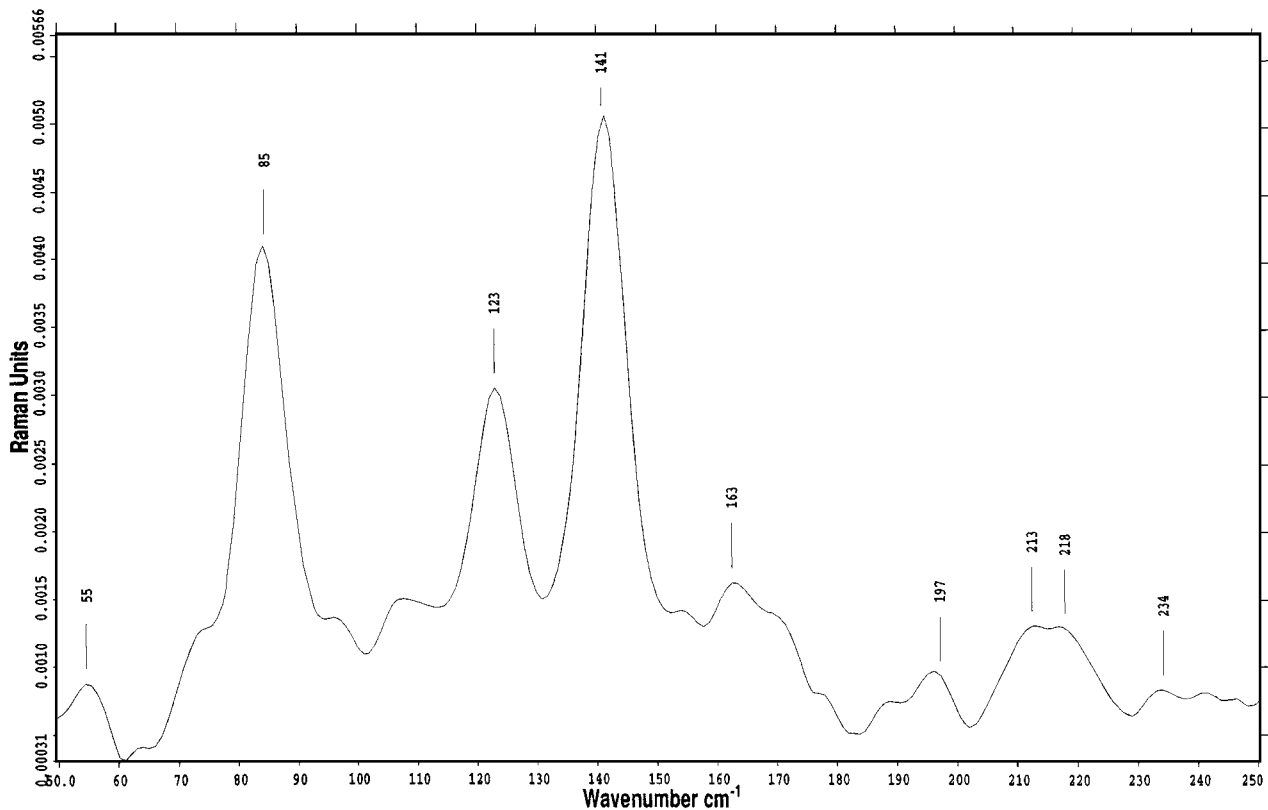*Figure 3* Decomposition of the Al2p peak and the Cu3p peak.

Figure 4 Raman diffusion spectra of a $CuAlTe_2$ film obtained at 670 K.

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