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Structural investigation of electrochemically synthesized ZnCuTe thin films

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Abstract pZnCuTe thin films were prepared by electrochemical synthesis in aqueous solution. Cyclic voltammetric analysis allowed us to single out the potential region where deposition of the species occurs. Upon annealing at 400 °C, formation of cubic ZnCuTe was confirmed by X-ray diffraction. The patterns were modelled using a MarqX algorithm which allows direct refinement of lattice parameters over the entire pattern instead of single-peak profile analysis.

Keywords ZnCuTe films · Semiconductors · X-ray diffraction · Cyclic voltammetry · Electrodeposition

Introduction

Electrochemical synthesis has been demonstrated to be a suitable procedure to prepare ZnTe thin films [1, 2]; these have been previously investigated in the light of their electro-optical properties as p-type conductive materials for photovoltaic applications [1, 2, 3]. Alloying of ZnTe with Cu gives rise to modifications in structural as well as optical characteristics of the binary compound, as revealed by previous X-ray diffraction (XRD) and optoelectronic characterizations [3, 4, 5].

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It was found that Cu produces a variation in the optical characteristics of ZnTe in terms of the absorption coefficient; the energy gap value of the ternary compound (1.7 eV) appears to account for the presence of additional electronic levels introduced by copper in the ZnTe band gap, close to the valence band edge [3, 4, 5]. Formation of the ternary ZnCuTe compound was revealed by a shift of the (111) reflection of the cubic structure in the XRD pattern with respect to ZnTe and Cu₂Te [6].

However, in order to determine precise lattice parameters of the phases obtained upon thermal treatment of the electrodeposited films, and excluding any possible contribution of Zn-Te and Cu-Te mixed phases, an X-ray study was made using a profile-fitting program able to model the whole patterns of the films. This program uses pseudo-Voigt curves (weighted averages of Lorentzian and Gaussian curves) to model diffraction peaks, including the $K\alpha_1/K\alpha_2$ doublet and a polynomial for the background. The advantage of using MarqX over conventional profile-fitting programs is that it is possible to directly refine lattice parameters for the present phases instead of single-peak positions, in order to satisfy the appropriate weight scheme connected with the statistical weight of the observed XRD data points. Such an approach is probably the best in a case like the present study, where no internal standard can be used; in addition, the lattice parameters of the SnO₂ (cassiterite) interlayer cannot be taken as a reference because of the peculiarity of the thin films (possible residual strain effects and unknown stoichiometry; possible contamination).

Experimental

Electrodeposition of ZnCuTe thin films on fluorine-doped tin oxide (SnO₂:F) substrates was carried out at room temperature in an aqueous bath. The solution contained 15 mM ZnCl₂, 1.5 mM TeO₂ and different CuCl concentrations (0.01, 0.1 mM). The pH of the solution was adjusted to a value of 2 by addition of appropriate amounts of 0.1 M HCl. The working electrode was 0.4 μm thick

SnO₂:F covered glass (sheet resistance: 10 Ω sq⁻¹). Electrical connection was established by means of a silver conductive paste. Before use, tin conductive oxide substrates (TCO) were treated for 5 min with ultrasonic waves in a bath of isopropanol and then rinsed with acetone. The reference saturated calomel electrode (SCE) was placed as close as possible to the working electrode. A large-area Pt foil was used as the counter electrode. The potentiostatic deposition was carried out at -0.75 V vs. SCE [3]; it was stopped when a charge of 2 C/cm² was passed through the circuit. The electrodeposition mechanism was investigated by cyclic voltammetry (CV); a three-electrode cell was connected to an AMEL electrochemical set-up. Cyclic voltammograms were carried out at a sweep rate of 20 mV s⁻¹, with the potential scanned first in the negative direction. Annealing of the films was carried in an argon flux at 400 °C for 10 min.

XRD analysis was performed with a Philips X'Pert thin-film diffractometer at a low angle of incidence (0.5°) to improve the quality of information from the top layer. Profile fitting was done using MarqX, a computer program for whole pattern analysis of XRD powder data. A further advantage of using such a program is in the relative insensitivity to the presence of unaccounted reflections from secondary phases. As shown in the following, the presence of unknown phase reflections does not affect the quality of the fitting and in particular the refined value of the lattice parameter for the two main phases: cubic Cu-Zn telluride and SnO₂ (cassiterite).

The composition of the thin films was analyzed by an energy-dispersive X-ray (EDAX) microanalytical unit of a scanning electron microscope (Philips XL 20) operating at an accelerating voltage between 15 and 20 kV. Various measurements were carried out on different regions of the deposited films, and the average composition was determined. Concentration calculations were carried out using the ZAF intensity correction algorithm.

Results and discussion

Figure 1 shows the cyclic voltammograms for the electrodeposition baths with a Zn/Te molar ratio = 10. The Cu ions content was 0.0, 0.01 and 0.1 mM in the cycles denoted by a, b and c, respectively. In cycle a, the cathodic peak related to Te deposition (-0.45 V_{SCE}) precedes the cathodic wave of ZnTe deposition (-0.65 V_{SCE}). The large anodic peak at about +0.5 V_{SCE} denotes the stripping of the binary ZnTe compound; this latter progressively decreases in intensity in cycles b and c, denoting the competition for the deposition sites between copper and tellurium. At the same time, an anodic wave at lower potentials, slightly visible in cycle b, becomes a well-defined peak centered at +0.2 V_{SCE} in cycle c, revealing the oxidation process of elemental copper deposited at a cathodic potential of -0.32 V_{SCE}.

The voltammograms obtained at Zn/Te = 100 and Cu⁺ = 0.0 mM (cycle a), 0.01 mM (cycle b) and 0.1 mM (cycle c) are shown in Fig. 2. With respect to the previous voltammogram, oxidation of Te ions (stripping of ZnTe) in the absence of Cu ions (cycle a) is denoted by a low-intensity wave starting at ~0.3 V_{SCE}; a slight increase in current is observed for Cu⁺ = 0.01 mM (cycle b); similarly to the electrodeposition experiments at Zn/Te = 10, a definite peak related to the oxidation of copper appears in cycle c at a lower potential (+0.2 V_{SCE}), where a high concentration of Cu ions allows the

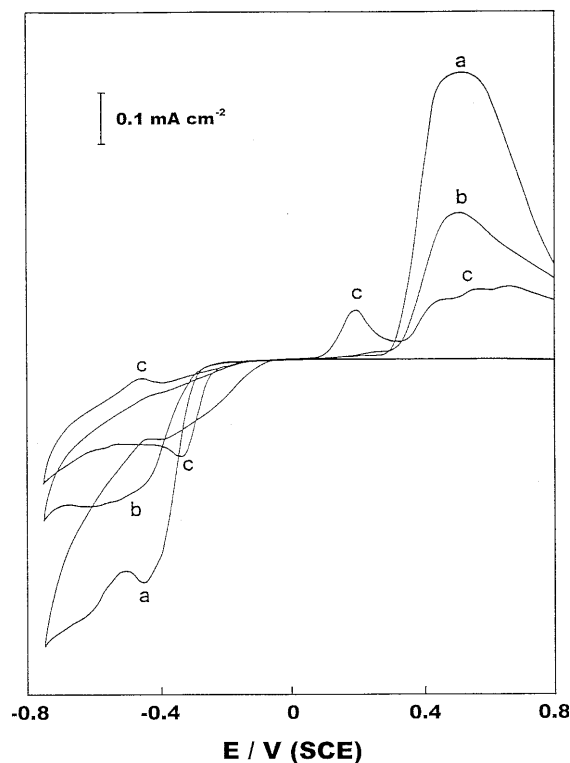


Fig. 1 Cyclic voltammograms of TCO in aqueous solution (pH = 2) with Zn/Te molar ratio = 10 and different CuCl amounts in the electrodeposition bath: (a) 0.0; (b) 0.01 mM; (c) 0.1 mM

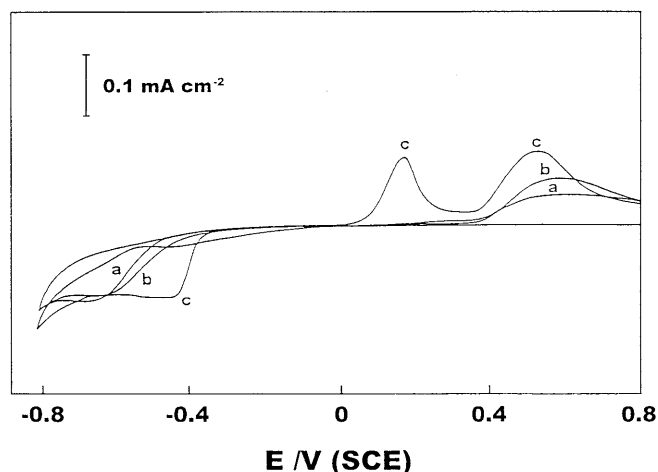
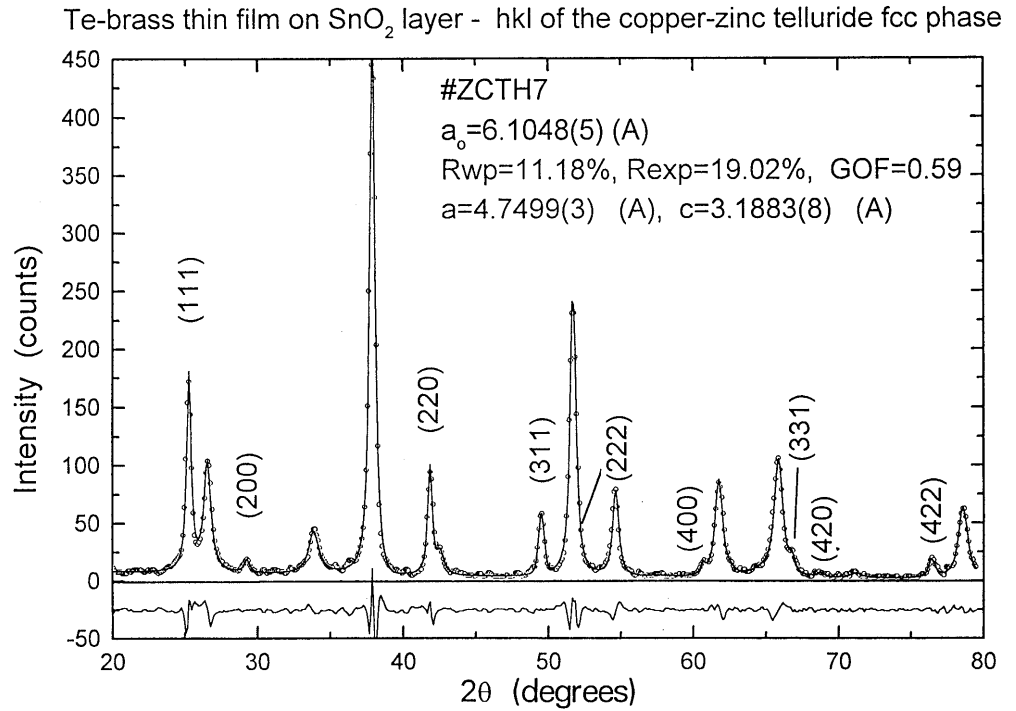


Fig. 2 Cyclic voltammograms of TCO in aqueous solution (pH = 2) with Zn/Te molar ratio = 100 and different CuCl amounts in the electrochemical bath: (a) 0.0; (b) 0.01 mM; (c) 0.1 mM

simultaneous formation of copper telluride. The above CV experiments allowed us to single out, from the anodic stripping peaks, the cathodic potential region where deposition of the ZnTe and Cu₂Te phases occurs. Accordingly, formation of Cu₂Te starts at -0.4 V_{SCE} whereas ZnTe deposition takes place at about -0.75 V_{SCE} and appears to be thermodynamically favored at lower potentials. Predetermination of the deposit composition can be achieved by appropriate choice

Fig. 3 XRD modelling results of sample ZCTH7



of deposition potential and concentration in terms of Zn/Cu and Zn/Te ratios. On this basis, the ZnTe phase containing a Cu amount corresponding to the concentration used in the bath was deposited at a cathodic potential of $-0.75 V_{SCE}$. To obtain a film having $\sim 1 \mu\text{m}$ thickness, a deposition charge of 2 C/cm^2 was adopted.

Figure 3 shows the results of the modelling for sample ZCTH7: the experimental pattern (open circles) is shown together with the modelled pattern (line) and the difference (residual, line below). The statistical indexes [7] of the fitting indicate a good quality of the results, which are reported in Table 1, including the errors (estimated standard deviations) in parentheses.

The same quality of fitting was also obtained for ZCTH10 (Fig. 4), but the statistical indexes were somewhat higher for samples ZCTH3 and ZCTH400. All the expected fcc lines were observed; consequently, no significant texture is present in the CuTe phase. Stronger (hhh) lines were found in ZCTH400 only, possibly indicating a weakly preferred orientation along the corresponding direction.

For ZCTH3 and ZCTH400, as shown in Figs. 5 and 6, the quality of the modelling was worsened by the presence of a few minor reflections from an unidentified

phase. It can be visibly appreciated, however, that these impurity phase peaks do not affect markedly the modelling of the reflections from the Cu, Zn, Te brass phase, which is the true object of this study. The effect can be seen in the increased error (lower precision) in the lattice parameter reported in Table 1, at least as far as precision is considered, i.e. concerning random errors. The low GoF (< 1) is partly due to the presence of unassigned lines, but also to the relatively high background produced by Cu fluorescence that cannot be filtered by the crystal analyser (same wavelength as the incident X-ray beam). However, the lattice parameters and overall quality of the fitting are not significantly affected.

In summary, we can therefore rely on the lattice parameters reported in Table 1, at least as far as precision is considered, i.e., concerning random errors. As discussed above, in this case it is clearly impossible to add an internal standard, so systematic errors due to instrument and sample alignment cannot be ruled out completely. However, the lattice parameter values for the brass phase are reasonable when compared with the extreme terms, corresponding to cubic ZnTe ($a=6.1026 \text{ \AA}$) and Cu₂Te ($a=6.11 \text{ \AA}$) [8]. A fine agreement is not possible owing to possible effects of residual strain (in both ZnCuTe and SnO₂ films), unknown stoichiometry and contamination that can affect the observed values.

The films electrodeposited at different Zn/Cu ratios and annealed at different temperatures were analysed by EDAX. A typical spectrum (sample ZCTH10 in Table 2) is given in Fig. 7, showing the emission lines of Zn ($K\alpha$ and $L\alpha$), Cu ($K\alpha$ and $L\alpha$) and Te ($L\alpha$); in the same figure, peaks related to Sn ($L\alpha$), coming from the TCO

Table 1 Lattice parameters of ZnCuTe and SnO₂ phases

Sample	Cubic Cu-Zn telluride (Å)	SnO ₂ (cassiterite)	
		a (Å)	c (Å)
ZCTH10	6.1077(4)	4.7479(3)	3.1844(8)
ZCTH7	6.1048(5)	4.7499(3)	3.1883(8)
ZCTH3	6.1003(6)	4.7437(3)	3.1870(8)
ZCTH400	6.0940(6)	4.737(1)	3.197(2)

Fig. 4 XRD modelling results of sample ZCTH10

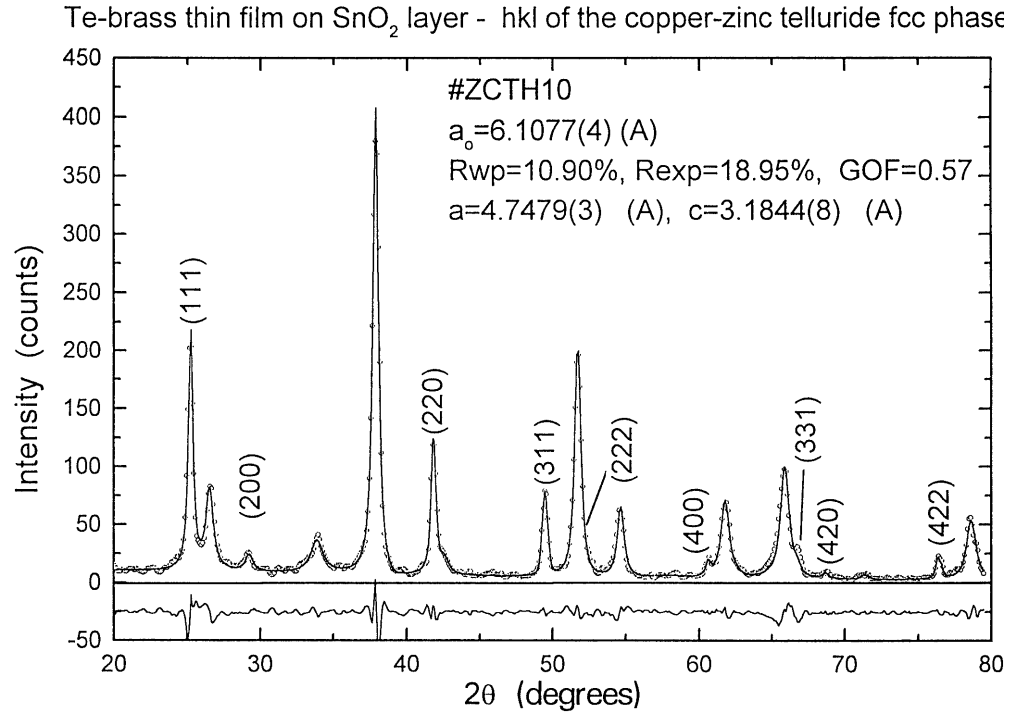
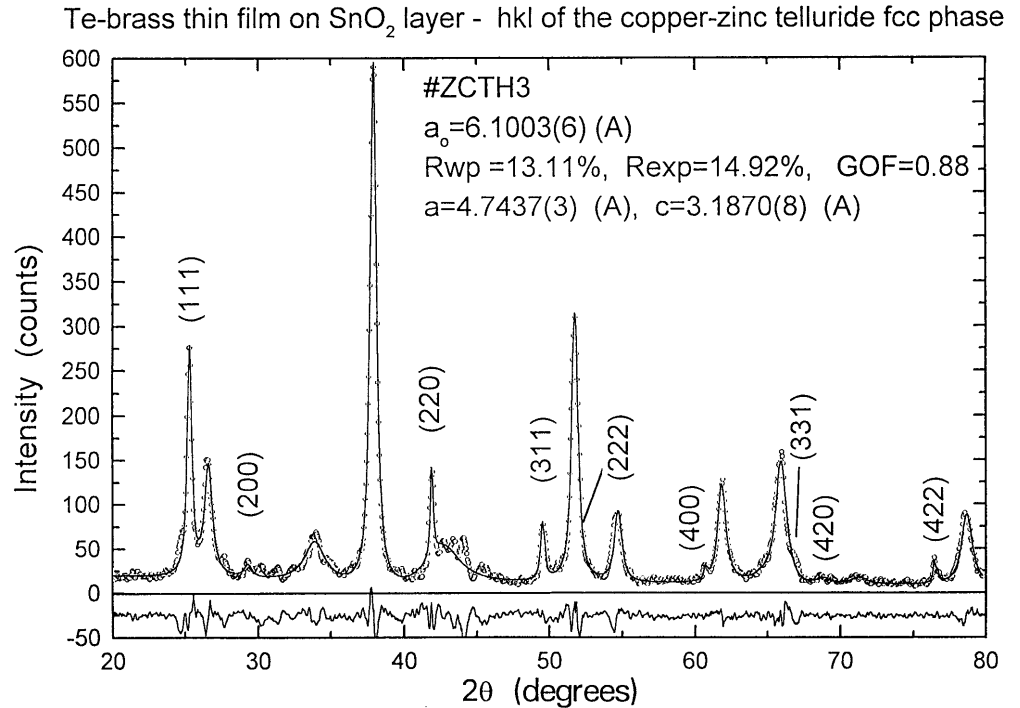


Fig. 5 XRD modelling results of sample ZCTH3



substrate, and Si ($K\alpha$), coming from the glass substrate, are also shown. The overlapping of the Sn ($L\alpha$) and Te ($L\alpha$) peaks does not allow the determination of the Cu+Zn/Te ratio in the films; thus, only the Zn/Cu values are reported in Table 2. These qualitatively agree with the different bath compositions adopted during the electrodeposition experiments, i.e. the Zn/Cu ratio in the films decreases with the increase of the Cu content in the bath.

Conclusions

ZnCuTe films were successfully electrodeposited on tin oxide substrates in aqueous solution under potentiostatic control. CV analysis indicated the potential region where simultaneous deposition of both ZnTe and Cu₂Te occurs. The composition of ZnCuTe films can be tuned by changing the Zn/Cu ratio in solution at

Fig. 6 XRD modelling results of sample ZCTH400

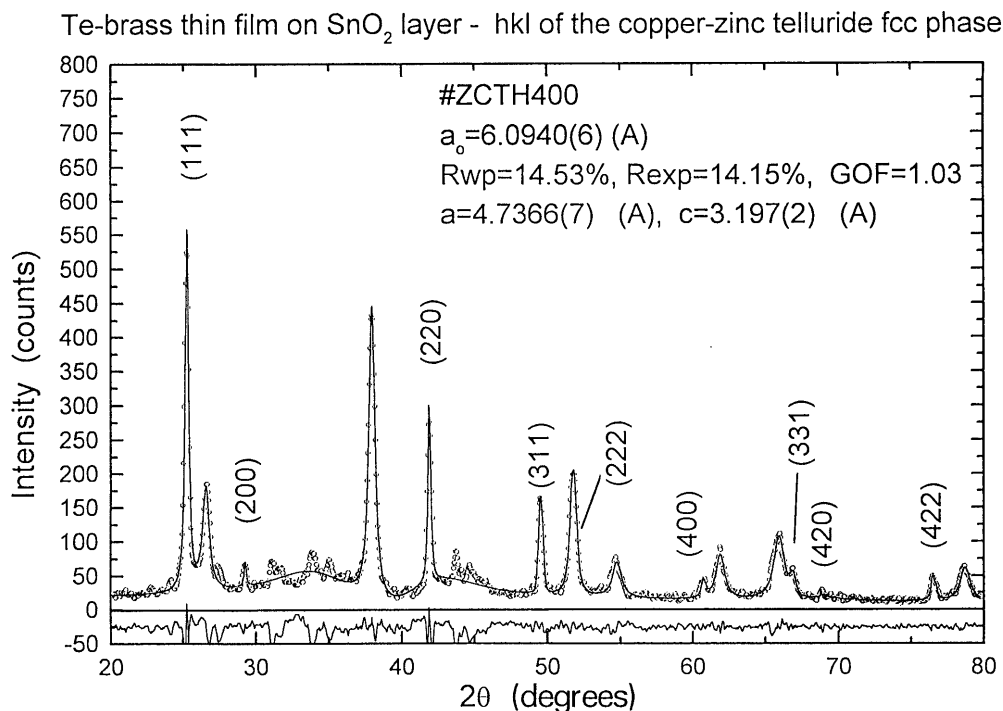


Table 2 Preparation and composition data of the films

Sample	Zn/Te molar ratio	Cu concentration in the electrodeposition bath (mM)	Zn/Cu ratio in the film by EDAX
ZCTH10	10	0.01	4.0
ZCTH3	100	0.01	2.33
ZCTH400	10	0.1	2.03
ZCTH7	100	0.1	0.54

the fixed potential of $-0.75 V_{SCE}$. After annealing, the films showed a crystalline cubic structure, related to a ternary ZnCuTe compound, identified through XRD analysis. Investigation of the semiconductive properties of the obtained films is ongoing in order to assess their applicability in photovoltaic, as well as sensor, devices.

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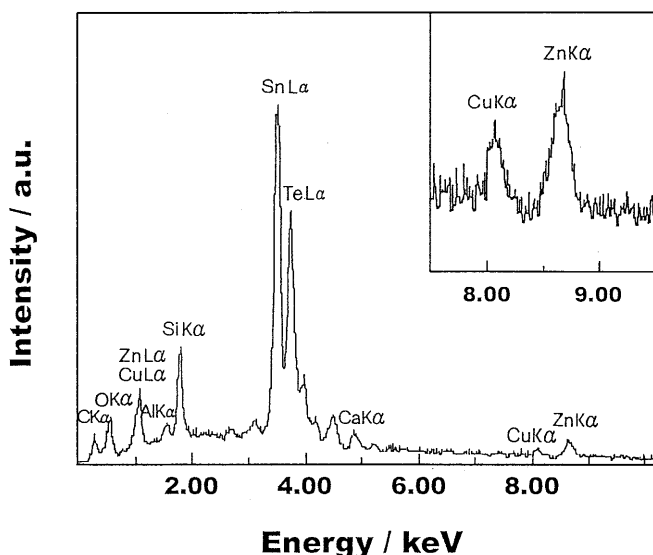


Fig. 7 EDAX spectrum of a typical Zn_xCu_yTe film on TCO (sample ZCTH10 in Table 2). The *inset* shows Cu K α and Zn K α on an expanded scale