Structural investigation of electrochemically synthesized ZnCuTe thin films

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].

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 Cu$_2$Te [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 Kα1/Kα2 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 SnO$_2$ (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 (SnO$_2$:F) substrates was carried out at room temperature in an aqueous bath. The solution contained 15 mM ZnCl$_2$, 1.5 mM TeO$_2$ 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 calmol electrode (SCE) was placed as close as possible to the working electrode. A large-area Pt foil was used as the counter electrode. The potential deposition was carried out at -0.75 V vs. SCE [3]; it was stopped when a charge of 2 C cm⁻² 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 out 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 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.