Semicond. Sci. Technol. **12** (1997) 1658–1661. Printed in the UK PII: S0268-1242(97)86243-8

# Characterization of $CuInTe_2$ thin films prepared by flash evaporation

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Received 22 July 1997, accepted for publication 18 September 1997

**Abstract.** Thin films of $CuInTe_2$ were grown by flash evaporation. The influence of the substrate temperature $T_s$ during film deposition on the properties of the thin films was examined. $CuInTe_2$ films were structurally characterized by the grazing incidence x-ray diffraction (GIXD) technique. Investigation by this technique demonstrates that the surface of thin films of $CuInTe_2$ prepared by flash evaporation at $T_s \geq 100$ °C exhibits the chalcopyrite structure with additional binary compounds in the surface. However, in the volume the films exhibit the chalcopyrite structure only; no foreign phases were observed. X-ray reflectometry was utilized to evaluate the critical reflection angle $\beta_c$ of $CuInTe_2$ ($\beta_c^{CuInTe2} \approx 0.32°$) which permitted us to calculate the density of the films to be $\rho \approx 6$ g cm$^{-3}$. The evaporated films were p type and the films deposited at $T_s = 100$ °C had a resistivity in the range 0.3–2 Ω cm. From optical measurements we have determined the optical energy gap $E_g \approx 0.94$ eV and the effective reduced mass $m_r^* \approx 0.07 m_e$.

## 1. Introduction

$CuInTe_2$ is a ternary chalcopyrite compound of the I–III–$VI_2$ family [1]. The Cu-III–$VI_2$ group has been extensively studied in recent years because of the potential applications in multijunction thin-film solar cells [2–5]. Polycrystalline thin-film heterojunction devices such as $ZnO/CdS/CuInSe_2$ showed high solar energy conversion efficiency, over 14% [6]. Certain compounds such as $CuInX_2$ (X = Te, Se, S) and $CuAlTe_2$ can be made both p- and n-type conductive [7–9]. $CuInTe_2$ has a high absorption coefficient ($\alpha \approx 10^4$–$10^5$ cm$^{-1}$) and an energy gap in the range 0.93–1.06 eV [8, 10–12]. $CuInTe_2$ can thus be used as an absorber layer in heterojunction devices with other I–III–$VI_2$ or II–$IV_2$ semiconductors [13].

Several workers [14–17] have reported investigations on the growth and characterization of thin films of $CuInX_2$ (X = Te, Se, S). To our knowledge there have so far been no reports on the characterization by grazing incidence x-ray diffraction (GIXD) and no reports on the $\beta_c^{CuInTe2}$ for $CuInTe_2$ thin films prepared by flash evaporation. These techniques allow us to study the surface of the films, which plays a prominent role in the formation of junctions between $CuInTe_2$ and other compounds.

We report here the results of an investigation of the structural properties of $CuInTe_2$ prepared by flash evaporation at substrate temperature $T_s = 100$ °C and characterized by GIXD and x-ray reflectometry techniques. Flash evaporation requires simple and inexpensive apparatus and gives thin films with acceptable quality at a reduced cost. These advantages are highly desired in the research into and fabrication of thin-film devices.

This study is complemented by optical transmission measurements. The spectral dependence of the absorption coefficient was obtained using a method previously reported by Bennouna *et al* [18].

## 2. Experimental details

$CuInTe_2$ powders used in the experiments were prepared by using constituent elements of 5N pure copper, indium and tellurium weighed in stoichiometric ratios. The mixture was sealed in an evacuated quartz tube. The sealed tube was placed in a horizontal furnace and the temperature was increased at the rate of 100 °C h$^{-1}$ up to 900 °C. The mixture was maintained at this temperature for a period of 40 h. It was then cooled to room temperature.

$CuInTe_2$ thin films were grown by flash evaporation of the fine-grained powder of $CuInTe_2$ from a molybdenum boat under a vacuum of $10^{-5}$ Torr onto glass substrates which were kept at various temperatures $T_s$. $CuInTe_2$ powders were fed into the preheated Mo boat from a mechanically vibrated powder-holder, both of which were contained in a conventional vacuum system. Thin films with a uniform thickness over an area in the order of 2 cm$^2$ were easily and repeatedly obtained with a substrate–boat distance of about 12 cm. The film thickness was

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measured with an interference microscope. Samples of various thicknesses (0.2–0.8 $\mu$m) were obtained.

The crystallographic properties of both the surface and the volume as well as the electronic density of $CuInTe_2$ thin films prepared by flash evaporation were determined respectively by GIXD and specular x-ray reflectometry. These experiments were made using a Siemens M386-X-A3 goniometer equipped with a copper x-ray tube anode (CuK$\alpha$).

The conductivity type of the samples was determined from the hot-probe measurements. The resistivity was measured using the four-probe technique. Indium, which is known to result in ohmic contact with $CuInTe_2$ [13], was used in these measurements.

The optical transmittance was measured with a Shimadzu UV 3101 PC Spectrophotometer.

## 3. Results and discussion

We note that the GIXD, x-ray reflectometry and optical measurements reported here are pertinent to samples obtained by flash evaporation at $T_s = 100$ °C. Similar results were observed at $T_s$ greater than 100 °C with a change in the value of the optical energy gap.

### 3.1. X-ray diffraction: properties of the volume

X-ray diffraction (XRD) was carried out on the films in order to confirm their crystallinity. Figure 1(a) shows the XRD pattern of $CuInTe_2$ powdered sample. All the peaks observed were attributed to the chalcopyrite phase. The XRD spectrum for a film deposited on an unintentionally heated substrate demonstrates that the as-deposited films were amorphous in nature. At $T_s \geq 100$ °C a single phase of $CuInTe_2$ thin films can be easily obtained (figure 1(b)), but no foreign phases such as In–Te and Cu–Te alloys or elemental components were observed. Consequently, the thin films of $CuInTe_2$ obtained by flash evaporation and deposited at substrate temperatures $\geq$100 °C exhibited a chalcopyrite structure in the volume.

### 3.2. Grazing incidence XRD: properties of the surface

Figure 1(c) shows GIXD spectra obtained at incidence angle $\beta = 0.25°$. The x-ray penetration depth at this angle is about a few tens of angstroms. So the spectrum of this figure indicates the structure of the surface of $CuInTe_2$ thin films. We note that the characteristic peaks of the chalcopyrite (112), (204) and (116) were present and this spectrum is marked also by the presence of additional peaks characteristic of binary compounds such as: $In_2Te_3$ and $Cu_2Te$. The presence of the binary compounds on the surface is observed in all the analysed samples. At this time it is not easy to propose a complete explanation of this behaviour, but it is due probably to a difference in the mobility of the different atoms on a heated substrate or to the loss of tellurium upon heating the substrate.

For $\beta \geq 0.45°$ the analysed depths are a few hundreds of angstroms. Figure 1(b) indicates the GIXD measurements at $\beta = 0.45°$ of the films deposited onto the

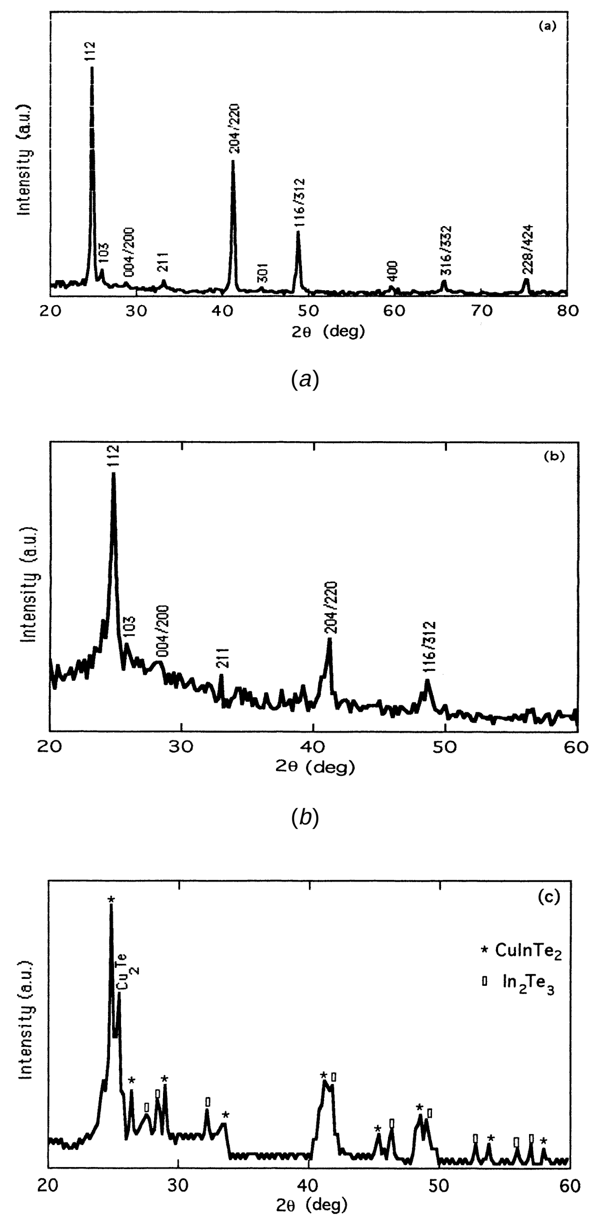


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**Figure 1.** (a) Powder diffraction pattern; (b) XRD spectrum of $CuInTe_2$ film deposited at $T_s = 100$ °C; (c) GIXD spectrum of $CuInTe_2$ at grazing angle $\beta = 0.25°$ ($T_s = 100$ °C).

heated substrate at $T_s = 100$ °C. This spectrum indicates the absence of the binary compounds in the volume and an enhanced crystallinity of the ternary alloys.

### 3.3. X-ray reflectometry

Figure 2 shows the variation of the specular reflected intensity as a function of the x-ray incidence angle. From this spectrum we can determine the critical angle for total internal reflection $\beta_c$.

It is well known that for x-rays, $\beta_c$ is related to the

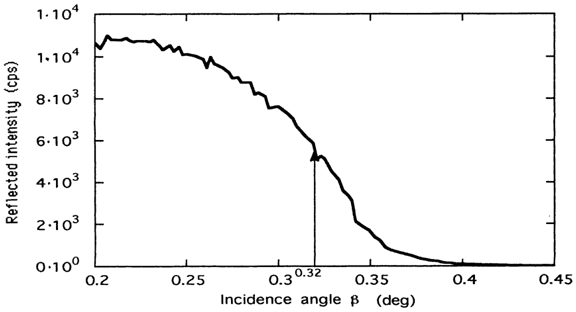


**Figure 2.** Reflectivity of the $CuInTe_2$ thin films deposited at $T_s$ = 100 °C.

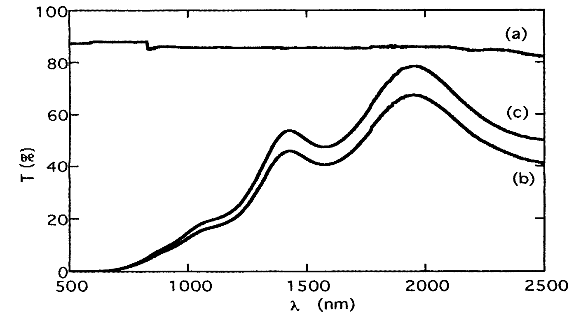


**Figure 3.** Transmission (in percentage) versus light wavelength: (a) of a substrate; (b) of $CuInTe_2$ thin film on substrate; (c) of $CuInTe_2$ (film deposited at $T_s$ = 100 °C).

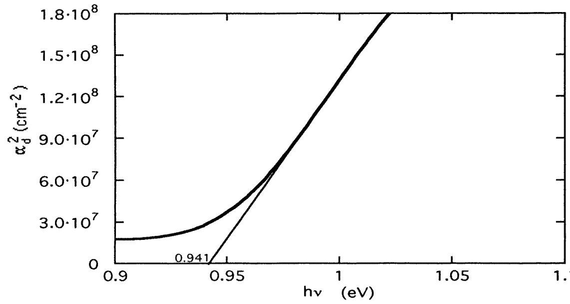


**Figure 4.** Dependence of the parameter $\alpha_d^2$ on the photon energy for a film deposited at $T_s$ = 100 °C.

density $\rho$ of the medium by the formula [19]

$$\beta_c^2 \approx 5.402 \times 10^{-6} \rho \lambda^2 Z/A$$

where $Z$ is the atomic number and $A$ is the atomic weight. In this expression the anomalous dispersion correction is neglected.

The calculated value of $\beta_c$ from the specular reflectivity data is $0.32° \pm 0.02°$ (figure 2) and the deduced value of the density of the $CuInTe_2$ film is $\rho \approx 6$ g cm$^{-3}$. This value is in good agreement with the density of bulk $CuInTe_2$ ($\rho = 6.04$ g cm$^{-3}$). This slight difference in the density is due probably to the presence of the binary phases on the surface which do not perturb the overall quality of the films.

### 3.4. Electrical properties

The $CuInTe_2$ thin films prepared by flash evaporation were found invariably to be p-type semiconductors from hot-probe tests. No changes in the type of conductivity were observed when the substrate temperature was changed. This is in accordance with the results of Sridevi and Reddy [20] who reported that $CuInTe_2$ is a naturally p-type semiconductor. The resistivity of the films deposited at $T_s = 100$ °C was in the range 0.3–2 Ω cm at room temperature. These values are in agreement with those reported by other workers [13].

### 3.5. Optical measurements

Optical transmission of $CuInTe_2$ thin films prepared by flash evaporation at $T_s = 100$ °C was measured at room temperature with non-polarized light at normal incidence in the wavelength range 320 to 3200 nm. The interference effect found in the spectral dependence of the transmittance was used to determine the spectral dependence of the absorption coefficient $\alpha$ by applying the method developed by Bennouna *et al* [18]. This method is based on exploring the interference fringes of the transmittance curve only to determine the refractive index and the thickness of the sample. The filtered transmission curve (without the interference patterns) is then used to determine the absorption coefficient of the sample [18]. It should be noted that no reflection measurements are needed in this method.

Figure 3(a) shows the transmission of a substrate, figure 3(b) a substrate with a $CuInTe_2$ thin film on it and figure 3(c) a $CuInTe_2$ film only.

It is known that the fundamental absorption for $CuInTe_2$ is due to allowed direct transitions [8–11]. The absorption coefficient $\alpha_d$ for direct transitions is defined by the following relation [21, 22]

$$\alpha_d = A^*(h\gamma - E_g)^{1/2}$$

where

$$A^* = C m_r^{*3/2}/n$$

and

$$C = \pi e^2 2^{3/2}/ch^2 m_e^* \varepsilon_0$$

is a constant, where $m_r^*$ is the effective reduced mass and $n$ is the index of refraction.

From the plot of $\alpha_d^2$ versus $h\nu$ (figure 4) we have determined the energy gap $E_g \approx 0.94$ eV. This is in agreement with literature data [8, 10–12]. We have determined also $A^{*2}$ (the slope of $\alpha_d^2$ versus $h\nu$), i.e. $A^{*2} = 2.3 \times 10^9$ (eV cm$^2$)$^{-1}$; this value compares well with the published values for $CuInSe_2$ [23] and GaAs [24].

Based upon a value of $n \approx 2.6$ [25] for thin films, the deduced value of the effective reduced mass $m_r^*$ is $0.07 m_e$, ($m_r^{*-1} = m_e^{*-1} + m_h^{*-1}$).

The absence of a sharp absorption edge (figure 4) can be attributed to the presence of binary compounds on the surface of the films. This is in accordance with the GIXD measurements which are performed at the x-ray incidence angle $\beta = 0.25^\circ$. However, no binary phases are detected with this technique in the volume of the samples as demonstrated by the XRD measurements.

## 4. Conclusion

$CuInTe_2$ thin films have been deposited by flash evaporation at different substrate temperatures. Films deposited on unintentionally heated substrates were amorphous. At substrate temperatures greater than 100 °C the GIXD spectra, taken at different incidence angles on the films, demonstrate the existence of the characteristic peaks of the chalcopyrite structure and the presence of the binary compounds on the surface of the films. However, in the volume no phase of any binary compounds or elemental components was detected by XRD. From the x-ray reflectometry spectrum we have determined the density of the $CuInTe_2$ thin film, i.e. $\rho \approx 6$ g cm$^{-3}$.

Electrical measurements demonstrate that the films were p type with a resistivity in the range of 0.3–2 Ω cm for films deposited at $T_s = 100$ °C.

From the optical measurements on the $CuInTe_2$ film prepared by flash evaporation at a substrate temperature $T_s = 100$ °C we have determined both the energy gap $E_g \approx 0.94$ eV and the effective reduced mass $m_r^* \approx 0.07 m_e$.


## Acknowledgments

The authors would like to thank Professor R Evrard (Université de Liège, Belgique), Professor A Bennouna and Dr Y Ijdiyaou (Université Cadi Ayyad, Morocco) for help in this investigation.


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