Journal of Engineering and Applied Sciences 2 (9): 1403-1407, 2007
ISSN: 1816-949X

Optical Characterization of $CuInTe_2$ Grown by Vertical Bridgman Technique

Ammar Messous and Brahim Belhouki
Laboratory of Growth and Characterization of New Semiconductors,
Department of Electronic, University of Ferhat Abbas, Sétif 19000, Algeria

Abstract: Recently, Photoacoustic Spectroscopy (PAS) technique has emerged as a valuable tool for the study of materials, like chemical and physical materials, in this study we reports on the optical properties of the photovoltaic material $CuInTe_2$ (CIT) as characterised by Photoacoustic Spectroscopy (PAS). Measured spectra of p-conducting CIT single crystals are given using a high resolution photoacoustic spectrometer of the gas-microphone type. The data is used to evaluate the absorption spectra, the band gap energy and ionisation energies of defects that have been observed in the tail of the spectra. The obtained Results confirm the efficiency of the technique in detecting the non-radiative defects known to dominate the properties of this compound. A discussion on the relation between the composition of the samples and the intrinsic defect chemistry in this compound is also given. Finally, we give a comparison between the results we have obtained and those published in the literature.

Key words: $CuInTe_2$, Chalcopyrite crystals, optical properties, photoacoustic spectroscopy, non radiative defects

INTRODUCTION

The chalcopyrite I-III-VI_2 compound semiconductors have received considerable attention in recent years due to their academic interest and also because of possible practical application in solar cells and potential applications in domains such optoelectronic devices, (Arun *et al*., 2005; Bouloufa *et al*., 2003; Haworth *et al*., 1980). However, despite the significant efforts devoted to improve the efficiency of devices based on these materials, this remains limited by the fact that the preparation of these materials with desirable electrical and optical properties is difficult because of the complex intrinsic defect structure of these compounds (Zedagi *et al*., 2003; Rincon and Wasim, 1987; Neumann, 1983).

The influence of growth parameters and the subsequent etch conditions on the electrical properties of I-III-VI_2 have been published in the literature (Haworth *et al*., 1980). However, there is no definite model through which the experimental results can be interpreted in the appropriate manner. In particular, the identification of the electrically active intrinsic defect remains an open question. $CuInSe_2$, $CuInS_2$, $CuGaTe_2$ and $CuInTe_2$ are actually attracting an increasing attention in the field of optoelectronic devices. For example, thin film solar cell employing $Cu(In,Ga)Se_2$ (CIGS)-based absorber layers have achieved efficiencies in excess of 19,5%. It is suggested that solar cells based on CIT as the absorber layer having a band gap around 1eV (at room temperature) which is near that of $CuInSe_2$ should give the same order of efficiency (Zedag *et al*., 1994). The PA spectra of a sample are very similar to the absorption spectra obtained by other conventional spectroscopic methods. However, the conventional methods are based on the detection of photons emitted and absorbed by the molecule/atoms of the sample where scattering and diffuse reflection are the major problems, while in the PA technique, scattering and diffuse reflection do not pose any problem, as this technique is based on the detection of the acoustic signal induced by the absorption of the photons by the sample. (Shiwani *et al*., 2006).

MATERIALS AND METHODS

The samples used in this research were all as-grown p-type conducting grown by using the vertical Bridgman technique (Haworth *et al*., 1980). Figure 1 shows the schematic diagram of the electric furnace used for the 3T-VB method. Elements Cu, In and Te were sealed in a quartz tube having dimensions of 14 mm Ô×250 mm under a vaccumù of ~ 10^{-6} Torr. The high temperature zone was heated to 1040°C and the low temperature zone was heated to to the temperature corresponding to a desired Te vapour pressure between 2 and 200 Torr, an kept at

Corresponding Author: Ammar Messous, Laboratory of Growth and Characterization of New Semiconductors, Department of Electronic, University of Ferhat Abbas, Sétif 19000, Algeria

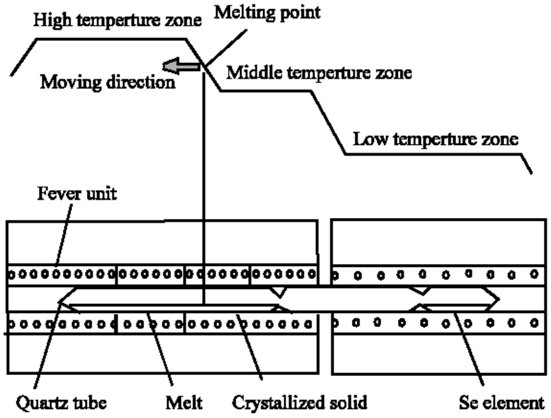

Fig. 1: Bridgman furnace

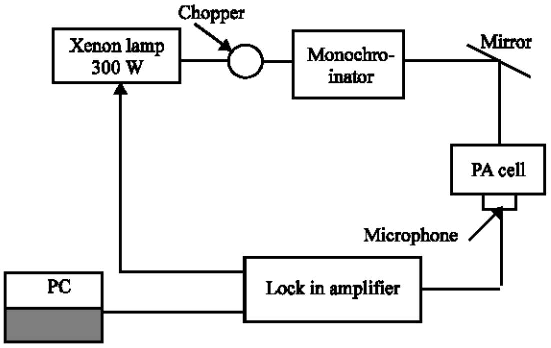

Fig. 2: Schematic diagram of the PA spectrometer

this temperature for 12 h for the formation of $CuInTe_2$ Compound. The middle temperature zone was maintained at 940°C during the crystal growth and then the temperature profile was moved at the speed of about 5 mm h^{-1}.

Crystals thus obtained were divided into three parts, i.e., "Top", "Middle" and "end". The "Top" denots the portion initially solidified. Since the "To" samples and the "End" samples contain high concentrations of defects.

Prior to being analysed, the samples chemically etched in a 1% bromine in methanol solution for 1 min and rinsed in de-ionised water.

The schematic diagram of the PA is shown in Fig. 2. In this diagram a Xenon 300 W short-arc lamp has been used as the radiation source. The light is chopped by a chopper at frequency interval f =10-500Hz. An mirror concentrates the light on the sample in the photoacoustic cell. An infrared filter is placed between the monochromator and the elliptic mirror in order to suppress the scattered light. A Brookdeal lock-in amplifier amplifies the detected photoacoustic signal from the microphone. The output of the amplifier is read with a keithley 175 auto-ranging digital voltmeter. A personal computer is used for the acquisition and the processing of PA data and to control the motor that drives the monochromator. The photoacoustic cell is cylindrical in shape containing the sample, the backing material and the gas. The schematic picture of a gas-coupled PA cell is shown in Fig. 3. All spectra were recorded at room temperature in the photon energy range hν = 0.7 to 1.4 eV. Finally, PA signal is corrected for the spectral distribution of the optical system and the cell by normalising the response of the sample to that of a fine powder of carbon black (Zedagi *et al*., 1994).

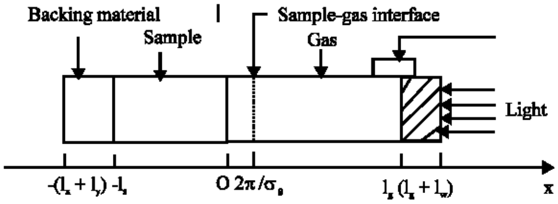

Fig. 3: Cross-sectional view of the sample cylindrical the positions of the sample, backing material and gas column

Photoacoustic spectroscopy principle: PAS is contact-less, non-destructive and unique in observing non-radiative de-excitation processes and offer the potential for depth profiling analysis. These properties led to a widespread use of this technique in many domains (Shiwani *et al*., 2006).

The main mechanism of the PA technique is the irradiation of a sample by sinusoidal chopped monochromatic light beam with a photon energy hν. Absorption of chopped light by samples is converted, in part or in whole, into heat by non-radiative de-excitation processes within the solid. This heat is generated inside of the region between the illuminated surface and the layer under the surface. This one deduced a disruption of the temperature and the pressure on the superficial layer of the sample that is detected by an acoustic or thermal mechanism or by the two. The produced signal is normalised and further processed using a personal computer.

Physically, the quantity of heat generated depends not only on the absorption and the efficiency of conversion coefficient of the material, but also of thermal diffusion coefficient of the material (Shiwani *et al*., 2006; Muller *et al*., 2006).

Coefficients of absorption and efficiency of the material in question give useful information on the expansion and the relaxation of the material. While, the thermal coefficient serves in the characterisation of the material (in measuring thermal properties of this material like the thermal diffusion and the thermal conductivity). The inconvenience remains the thermal and acoustic wave reflections by walls of the cell, notably in very elevated frequencies, what could produce interference and resonance phenomena inside the photo-acoustic cell (Shiwani *et al.*, 2006).

Defect formation energies: The deviation of the composition from the ideal formula I-III-IV_2 can be described by two parameters Δm and Δs, which determine the deviations from molecularity and valence stoichiometry, respectively. They are defined as:

$$\Delta m = \frac{|Cu|}{|In|} - 1 \tag{1}$$

$$\Delta s = \frac{2|Te|}{|Cu| + 3|In|} - 1 \tag{2}$$

Where |Cu|,|In| and |Te| are the total concentrations of Cu, In and Te atoms, respectively, in the compound.

The composition of CIT films used as absorbers in thin films solar cells is a topic of main importance since many cells properties are influenced by deviations from stoichiometry. Based on the defect chemistry model of ternary compounds proposed by Groenik and Janse (1978) the deviations from stoichiometric composition can be described by tow parameters Δm and Δs, which respectively determine the deviation from molecularity and stoichiometry (Muller *et al.*, 2006).

The meanings of deviations from zero for these parameters are described as follows:

- $\Delta m > 0$ Cu rich films (possibly secondary phase $Cu_{2-x}Te$)
- $\Delta m < 0$ In rich films (possibly secondary phase In, Te)
- $\Delta s > 0$ excess of selenium
- $\Delta s < 0$ selenium deficiency .

From the electrical measurement a shallow level around 15 meV has been reported (Rincon and Wasim, 1987). The published data of partial vapour pressure below the melting point of different compounds indicates that samples grown from the melt possess a deviation from both molecularity and valence stoichiometry characterised by $\Delta m < 0$ a $\Delta s < 0$. The majority defects which can be formed are due to Cu_{In}, V_{In}, In_i, Cui In_{Cu} and V_{Te} (Haworth *et al.*, 1980).

Electrical properties of CIT have always been measured of samples p-type conducting. The measurements have established that the concentration of holes is not essentially changed during the etching procedure. But, it has been observed that an increase in the degree of compensation occurred and therefore in the total concentration of donors and acceptors. If we assume that Cu interstitial and Te vacancies are the predominant intrinsic defect formed during etching procedure. We can conclude that the quantity of production of these two defects is nearly equal.

RESULTS AND DISCUSSION

The conductivity type of all the samples is determined using the thermal probe and were found to be p-type conducting. The elemental composition, as determined by energy dispersive X-ray fluorescence spectroscopy has given for almost all the samples that we have analysed the following composition: Cu: 22.4%, In: 26.5%, Te: 51.1% with an estimated error of ±10%. The optical properties (absorption coefficient spectra) are deduced from PA signals.

Photoacoustic spectra as function of the photon energy as measured are shown in Fig. 4. The spectra shows clearly the direct nature of the band to band transition edge together with peaks at energies between 0.7 and 0.9 eV which are associated with transitions between defect states and the conduction/valence bands (Fig. 5).

The analysis of data indicates that the relation which can describe the absorption spectra near the band gap for hí > E_g is expressed with the formula:

$$(\alpha h\nu)^2 = (h\nu - E_g) \tag{3}$$

From PA spectra, it is clearly observed that CIT is a direct semiconductor with a direct gap. Figure 6 and 7 show variations of $(\alpha h\nu)^2$ as a function of the photon energy. From these figures the energy gap of two samples

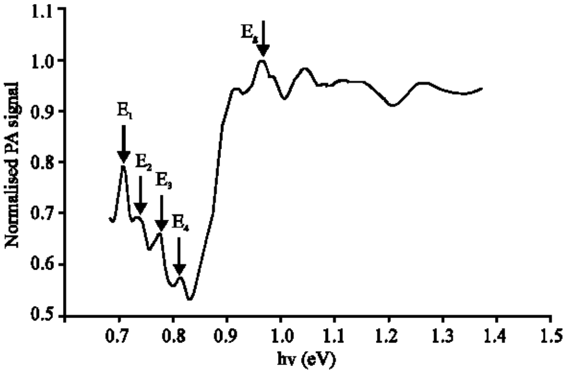

Fig. 4: Photon energy distribution of the normalised PA signal as measured of sample 1

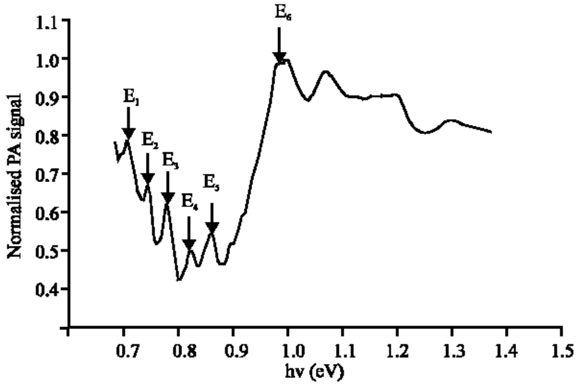

Fig. 5: Photon energy distribution of the normalised PA signal as measured of sample 2

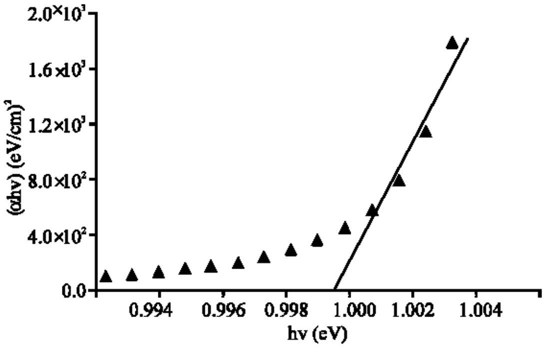

Fig. 6: Plot of $(\alpha h\nu)^2$ as a function of the photon energy hν for sample1

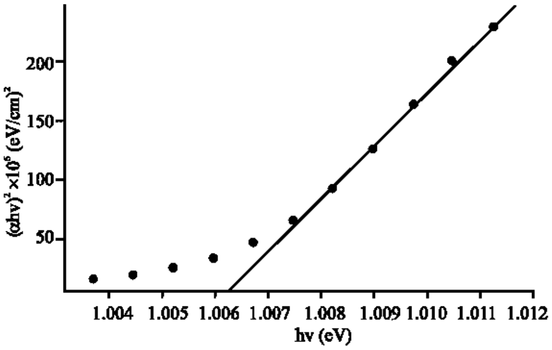

Fig. 7: Plot of $(\alpha h\nu)^2$ as a function of the photon energy hν for sample 2

is determined. For sample 1, $E_g \approx 0.9987$ eV and for sample 2, $E_g \approx 1.0065$ eV

Analysis of the experimental data shows that for all samples the linear portion of the plots is due to an allowed direct transition.

Ionisation energies of intrinsic defects are derived from the appropriately determined values of the gap energy. The values found are given in Table 1 with values of ionisation energies for intrinsic defect states as reported in the literature.

Table 1: Defect ionisation energies and the energy gap

	Sample 1	Sample 2	Literature
Eg (eV)	0.996	0.989	0.93-1.06
E1 (meV)	245	237	250 [3]
E2 (meV)	218	214	200 [13]
E3 (meV)	181	174	135-150[3]
E4 (meV)	139	138	-
E5 (meV)	109	-	75-90 [3.7]

Different energy levels have been observed in CIT after optical measurements: The shallow level 15 meV assigned to the antisite defect Cu_{In} (Haworth *et al.*, 1980; Rincon and Wasim, 1987), the levels 75 and 60 meV assigned to the vacancies of Cu (V_{Cu}) and to the vacancies of Te (V_{Te}), respectively (Yakushev *et al.*, 1995; Rincon and Wasim, 1997). In general, the conductivity p-type is always governed by the superficial acceptors possessing an ionisation energy that varies in the interval E_A=10-25 meV. Yakushev *et al.* (1995) have identified the existence of deep energy levels where their values vary in the intervals (75-90 meV), (135-150 meV) and (350-500 meV). These values are in good agreement with the values measured in this paper. Comparison between values found here and those published in the literature indicate that photoacoustic spectroscopy can be used as a reliable method to reveal the presence of populations of deep defects in CIT.

CONCLUSION

Photoacoustic spectroscopy has been used successfully in the study of the optical properties of p-type conducting $CuInTe_2$ single crystals. Shallow and deep non-radiative transitions have been detected. The gap energy has been determined and is found to be around 1 eV with an estimated error in precision of ± 5%. The defect ionisation energies of the defect populations observed in the absorption tail are found to be comparable to those published in the literature.

REFERENCES

Arun Vijayakumar, T.D. Kalpathy and B. Sundaram, 2005. Applied Surface Sci., 242: 168.

Bouloufa, A., A. Messous, M.V. Yakushev, R.D. Tomilson and A. Zegadi, 2003. J. Elec. Devices, 2: 34.

Groenink, J.A. and P.H. Janse, 1978. Z. Phys. Chem. 110: 17.

Haworth, L.I., R.D. Tomlinson and I.S. Al-Saffar, 1980. Jpn. J. Applied Phys., 77: 19-3.

Müller, J., J. Nowoczin and H. Schmitt, 2006. Thin Solid Films, 496: 364.

Neumann, H., 1983. Cryst. Res. Tech., 18: 483.

Rincon, C. and S.M. Wasim, 1987. Ternary and Multinary Compounds. S.K. Deb *et al*. (Eds.), MRS, pp: 443.

Rincon, C., S.M. Wasim, G. Marin and G. Sanchez Perez, 1997. J. Applied Phys., pp: 82.

Shiwani Pandhija, Nilsh K. Rai, A.K. Singh, A.K. Rai, R. Gopal, 2006. Progress in Cristal Grozth and Characterizition of Materials, 52: 53.

Yakushev, M.V., H. Neumann and R.D. Tomilson, 1995. Crist. Tech., 30: 121.

Zegadi, A., A. Bouloufa, N. Mazouz, B. Barka, E. Ahmed, R.D. Pilkington, A. E. Hill and R. D. Tomlinson, 2002. PV in Europe, Rome (Italy) 83: 7-11.

Zegadi, A., M.A. Slifkin and R.D. Tomlinson, 1994. Rev. Sci. Instrum., 65: 2238.