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Transmission Photoacoustic Spectroscopy Analysis of $CuIn_{0.75}Ga_{0.25}Se_2$ Thin Films

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Photoacoustic spectroscopy (PAS) has proved to be an effective technique for the evaluation of the inherent defect population in a wide range of materials for various applications. This paper demonstrates the use of this technique in transmission mode, and hence, evaluates the optical properties of flash-evaporated $CuIn_{0.75}Ga_{0.25}Se_2$ (CIGS) thin films. Both the photoacoustic and transmission spectra were recorded at room temperature using high-resolution near-IR of the gas-microphone-type PAS, which revealed a very broad transmission region (about 300 meV) near the fundamental band edge in the as-grown CIGS thin films due to the presence of several shallow defect levels. The postdeposition heat treatment of the samples under Se ambient, followed by annealing under inert and forming gas ambient, showed significant changes in the behavior of the PAS spectra, particularly near the fundamental band edge. The absorption coefficient has been derived from these spectra to determine the energy band gap values and the activation energies for several defect related energy levels. Using PAS, the energy band gap values were in the range of 1.197 to 1.202 eV. The optical transmission spectra were also recorded from the routinely used spectrophotometer. The transmission data was used to determine the energy band-gap values, which were calculated to be in the range from 1.159 to 1.194 eV. These values were found to be in good agreement with each other, as well as with values reported in the literature.

Keywords acoustics, copper alloys, electrical conductivity, semiconductors, solar cells, spectroscopy, thin films

1. Introduction

The polycrystalline thin film solar cells based on the chalcopyrite compound $CuIn/GaSe_2$ semiconductor have been produced with a record solar conversion efficiency of more than 19% (Ref 1), and studies are still in progress all over the world to further improve this efficiency. Although $CuIn_{0.75}Ga_{0.25}Se_2$ (CIGS) appears to be a promising candidate for use in heterojunction solar cells, there is a lack of information regarding its electro-optical properties. Conventional methods, used to determine the optical properties of a semiconductor thin film, measure the transmission of the film as a function of wavelength in both the transparent and absorption region. Many authors (Ref 2, 3) have independently proposed different methods to estimate the optical constants, such as the optical band gap, absorption coefficient, and defect levels, of thin films using only the transmission spectra. There is currently an increased demand for the determination of optical absorption coefficients below the band gap energy of thin films, as valuable information on band tailing and defect states can be obtained. When using conventional optical absorption techniques, the derived transmittance spectra can be misinterpreted. This could be due to either neglecting or incorrectly considering light scattering effects caused by surface roughness, grain boundaries, variations in film thickness, compositional inhomogeneities throughout the film, and by the use of inaccurate values of the refractive index of both the film and the substrate.

All the above problems can be avoided if the contactless, nondestructive, photoacoustic spectroscopy (PAS) technique (Ref 4) is applied to measure the optical absorption spectra. In this approach, only the absorbed light, which is converted into heat, contributes to the measured spectra (Ref 4). This technique relies on the generation of an acoustic signal when a sample, placed inside a closed cell, is illuminated with chopped monochromatic light. The measured acoustic signal, detected by a sensitive microphone, is a function of the optical absorption properties of the sample. PAS has proved to be an effective technique for evaluating not only the standard optical properties but also inherent shallow and deep level defects in a wide range of materials (Ref 5). For single crystals or thick films, where the thermal diffusion length is less than the thickness of the sample, the PAS signal is proportional to the absorption coefficient. However for thin films, where the thermal diffusion length is greater than the film thickness, the effects of the substrate and the multiple reflections within the film have to be taken into account.

In this paper, it is demonstrated that the same PAS system can be used both in the photoacoustic and transmission modes to gain detailed information, including deep and shallow defect level states and the energy band gap of semiconductor materials, and in particular, CIGS compounds in thin film form. The samples were deposited using a modified flash evaporation technique onto glass substrates. The effect of deposition temperature and the postdeposition annealing under various ambi-

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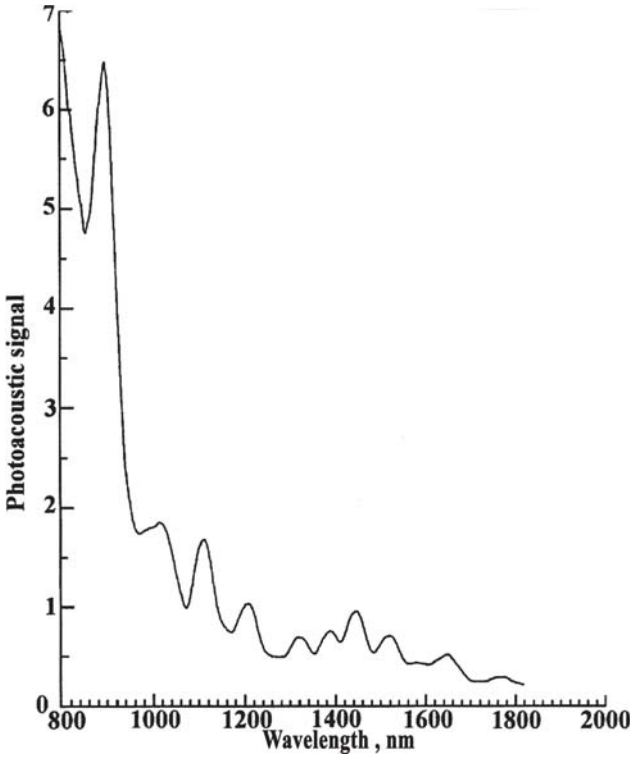

Fig. 1 Photoacoustic spectrum of the standard carbon black powder

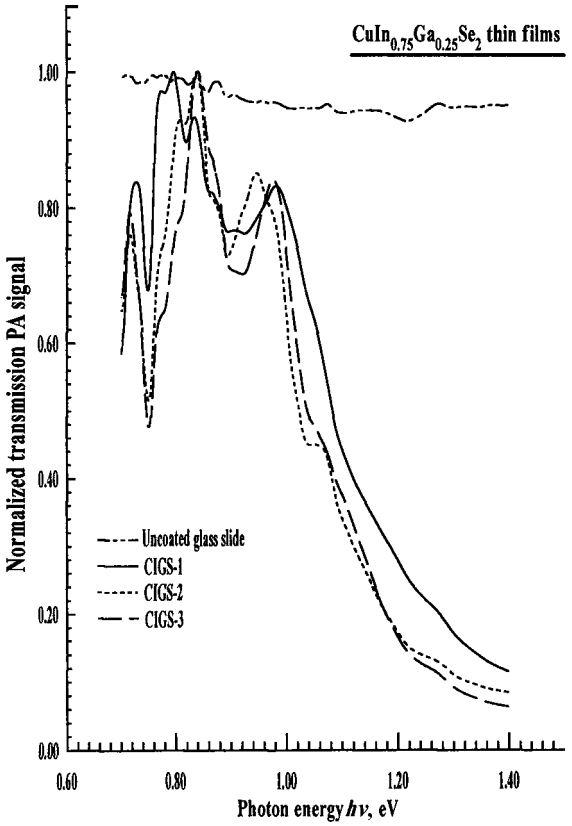

Fig. 2 Normalized transmission photoacoustic spectra of virgin glass slide and CIGS thin films

ent conditions have been examined at different temperatures and times on the optical properties of CIGS thin film samples. Using a PAS system in transmission mode has produced identical results to those obtained using standard PAS.

2. Experimental Procedures

The PAS system was modified to operate in transmission mode. TPAS employs a gas-microphone-type detection cell, containing fine grain carbon black powder, which is covered by a suitable quartz window. The thin film or single crystal (200 μm thick) semiconductor sample is placed on top of the cell window and exposed to a monochromatic light source. The modulated light, after passing through the sample, is absorbed by the carbon black powder, which acts as a true light trap with a flat response at all wavelengths (Ref 4). The sample has the effect of filtering out certain wavelengths so that, when comparing the PA spectra obtained with that of the standard carbon black spectra, the missing values of wavelengths can be ascertained and related to absorption levels in the sample.

Using this setup, measurements were registered for the flash-evaporated CIGS thin films. Thin film samples were deposited by the modified flash evaporation technique onto glass substrates, the temperature of selected samples was varied between room temperature and 200 °C (Ref 6). These were compared with spectra recorded from clean virgin glass substrates and also with spectra recorded using the standard PAS technique. All the measurements were recorded at room temperature using a chopping frequency of 112 Hz and a photon energy range of 0.7 to 1.4 eV. The final output was read by a personal computer, which was also configured to control the monochromator. The photoacoustic spectra were corrected to account for the spectral distribution of the optical system, the cell geometry, and the microphone response by normalizing the output signal of the specimen to that of fine grain carbon black powder. The optical transmission spectra were also obtained from a Hitachi 2000 (Hitachi, Basking Ridge, NJ) double beam spectrophotometer in the wavelength range from 800 to 1800 nm.

Various postdeposition annealing regimes were adopted: annealing in vacuum, annealing in an inert gas, annealing in an ambient 9:1 mixture of N_2/H_2, and annealing in a Se atmosphere. The influence of various temperatures in the range of 200 to 500 °C was investigated for 30 min. Two stage annealing was then used to optimize the general properties, in particular, the optical properties of the CIGS thin films.

3. Experimental Results and Discussion

Figure 1 details the photoacoustic amplitude data obtained from the carbon black standard from which all other spectra of single-crystal and thin-film samples were normalized. The average particle size of the standard carbon black powder was in the range of 1 to 10 μm, and the spectra was measured at room temperature with a modulating frequency of 112 Hz in the wavelength range of 800 to 1800 nm.

Figure 2 illustrates the normalized transmission photoacoustic spectra of as-grown CIGS thin films (approximately 1 μm thick) as a function of photon energy $h\nu$. It can be seen that all the spectra are dominated by defect levels both near the fundamental band edge as well as in the low photon energy range. Because of the presence of one or more shallow defect levels close to the band edge, the nature of the fundamental band-to-

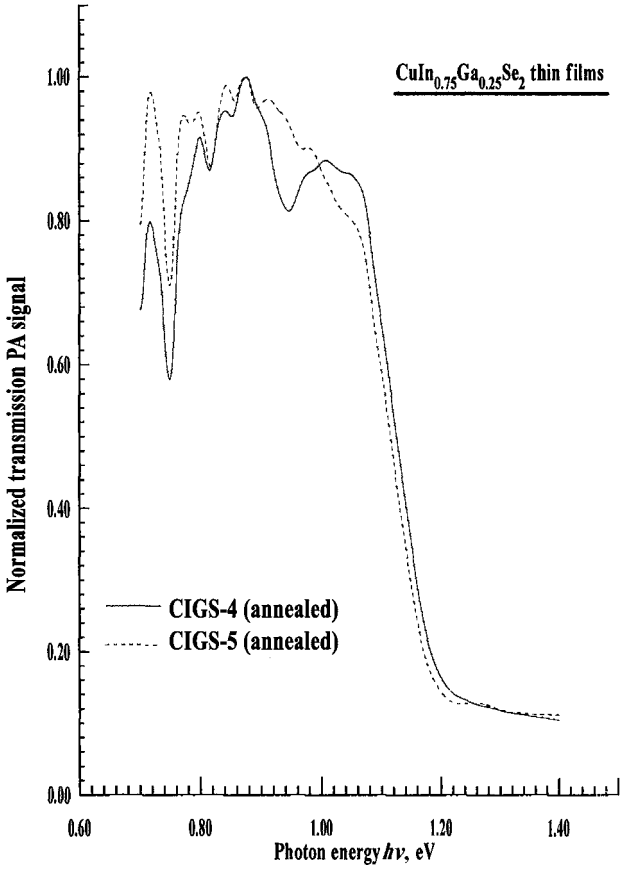

Fig. 3 Normalized transmission photoacoustic spectra of two stage annealed CIGS thin films

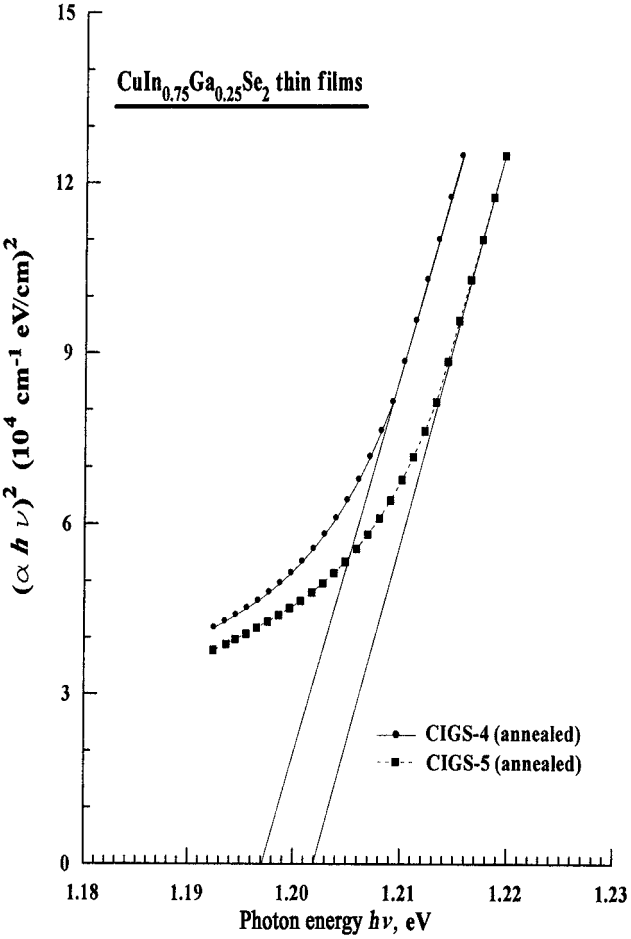

Fig. 4 Room temperature plots of $(\alpha h\nu)^2$ versus photon energy

band transition is difficult to establish as this region is extended across a 300 meV photon energy range. This was not surprising as the photoacoustic signal depends strongly on the structure and uniformity of the sample. In the case of thin films grown by flash evaporation for this work, the existence of voids and grain boundaries, and deviation from the stoichiometry (Ref 6), gave rise to these defects. The structural properties of the as-grown samples showed a preferred orientation in the form of a less intense and comparatively broad single ⟨112⟩ diffraction line, and the grain size was found to be less than 0.2 μm. The respective random Rutherford backscattering spectroscopy (RBS) spectra of these samples further confirmed the observed PAS results as they revealed a nonuniform composition through the depth of the film (Ref 6). In contrast, the normalized transmission photoacoustic spectra from the CIS and CIGS single-crystal samples always showed the region near the fundamental band edge to be free of defect states, therefore, displaying a steep transition edge (Ref 7).

To confirm that these transition peaks in the normalized transmission photoacoustic spectra are characteristic of CIGS thin films, a virgin 800 μm thick cleaned glass slide was also analyzed using the same setup. The normalized transmission photoacoustic amplitude signal recorded in the same photon energy range is plotted in Fig. 2 along with the spectra of thin films. It can be seen that the response is almost flat with an approximate 97% transmission across the energy range of interest with no major absorption peaks observed. An almost similar spectrum, to that of a cleaned glass slide, was observed from high-quality (approximately 99%) thin film of indium tin oxide (ITO) prepared by electron beam evaporation (Ref 8). These observations support the idea that the transitions in the low photon energy range of the normalized transmission photoacoustic amplitude signal of CIGS thin film are the characteristic of the sample as they do not appear in the photoacoustic amplitude spectrum of the virgin substrates.

The as-grown CIGS thin films when annealed under maximum Se vapor pressure at 300 °C for 120 min followed by an anneal in forming gas or Ar ambient at 200 °C for 30 min revealed significant changes in the transmission photoacoustic spectra. Figure 3 shows the resultant spectra of such CIGS thin films. One can note that the transition edge for annealed sample (CIGS-4) under forming gas ambient has fallen after that of the film (CIGS-5) annealed under Ar ambient. This apparent shift may be caused by the appearance of a broad dip at approximately 0.94 eV. Near the fundamental band edge the defect related shallow peaks disappeared and a clear indication of the band edge is now available. However, the peak position of the defect structure in the low photon energy range remains unaltered. The changes observed in the transmission photoacoustic spectra were found to be in good agreement with the improvements in the physical properties of the annealed sample (Ref 9). X-ray diffraction (XRD) spectrum showed a dramatic change in the film structure as the characteristic peaks of the chalcopyrite structure appeared. The RBS spectrum of the sample also confirmed improvements in the film uniformity and homogeneity as the excess surface indium was redistributed into the

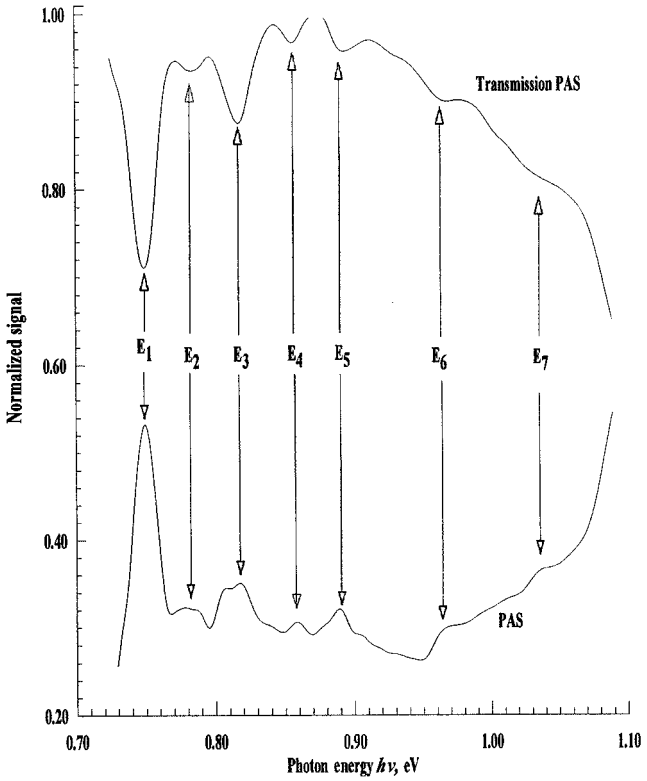

Fig. 5 Comparison of PAS and TPAS spectra of deep level transitions in CIGS thin films

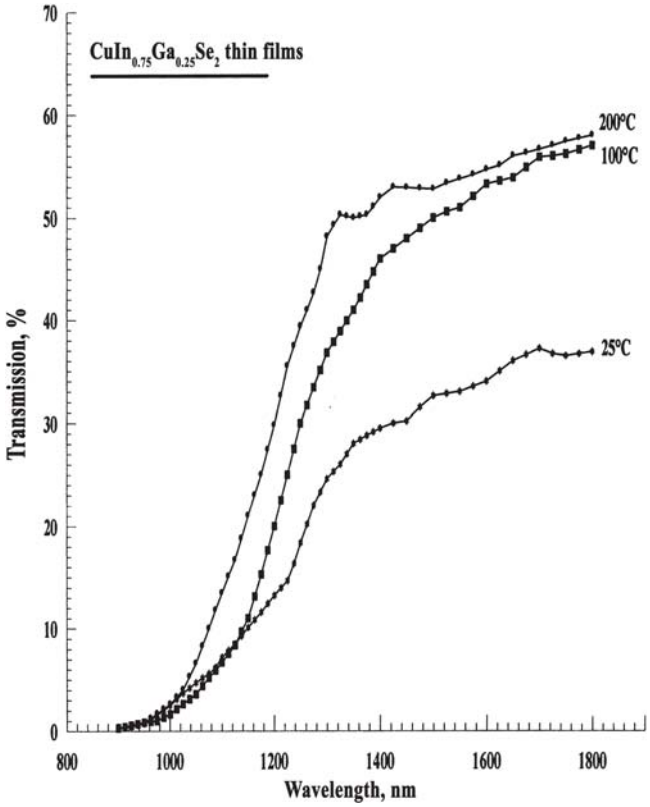

Fig. 6 Transmission spectra of CIGS thin films deposited at different substrate temperature

bulk along with the incorporation of selenium due to the annealing process. An increase in the grain size and corresponding decrease in the film resistivity have been measured together with an enhancement in the film composition towards that of the starting material. This indicates that the annealing process has resulted in the redistribution of the atoms and many of the defect states are annealed out.

The absorption coefficient calculated from the photoacoustic spectra of annealed CIGS thin films was used to determine the energy band gap from the room temperature plots of $(\alpha h\nu)^2$ against the photon energy $h\nu$, and the representative curves are shown in Fig. 4. By the extrapolation of curves to zero, the measured energy band gap value (~1.202 eV) of samples annealed in forming gas was found to be slightly higher than that observed (~1.197 eV) for Ar annealed thin film. The observed higher value of the energy band gap may arise for several reasons including the measurement error (~0.5%), compositional variations through the depth of the sample, or the appearance of some defect level. The possibility of this deviation caused by variations in composition with sample depth can be ruled out because the thickness of the sample in most of the cases was of the order of 1 μm, which is very small compared with the thermal diffusion length of 120 μm at the modulating frequency of 112 Hz. This would allow all the light to pass completely through the sample. Repeated transmission/photoacoustic measurements of the sample showed the same spectral behavior, therefore, the likelihood of measurement error can arguably be discarded. As discussed earlier, this observed deviation of energy band gap can largely be attributed to the appearance of a broad shoulder in the normalized transmission photoacoustic spectra (Fig. 5).

To compare the transitions observed in the low photon energy range from 0.7 to 1.10 eV, the normalized signal was measured using the spectrometer in photoacoustic and transmission modes and the acquired data is plotted in Fig. 5. In both cases, seven different peaks (labeled as E_1 to E_7) were observed at approximately 0.75, 0.78, 0.816, 0.857, 0.895, 0.96, and 1.035 eV, respectively. In the case of transmission photoacoustic spectra, these peaks are better resolved, indicating sharp transitions at their respective photon energy values. However, in photoacoustic spectra, the transitions are less pronounced, and some of the peaks (e.g., E_2 and E_3) appear to be a combination of two smaller peaks whose photon energy values are very close to each other. A similar type of spectrum was observed from CIGS single crystals (Ref 10), however, the intensity of the peaks was less in single crystal compared with those observed in thin films. Because the peak positions are the same in single crystals and thin films, their origin is also likely to be the same and can be attributed to transitions from one defect state to another, or transitions between defect states and the conduction or valence bands (Ref 11).

Figure 6 shows the transmission spectra of CIGS thin films deposited at various substrate temperatures. The spectrum of the film deposited at room temperature is smeared with a maximum transmission level of approximately 40%. However, the spectra representing films deposited at higher substrate temperatures were sharp with a higher maximum level of transmission approaching to 60%. These changes were found to be in good agreement with enhancements in the physical properties of the samples deposited at higher substrate temperatures or annealed after deposition (Ref 9, 12). This strongly indicates that, at higher temperatures, processes involving redistribution of atoms and the reduction of defects are occurring more rapidly.

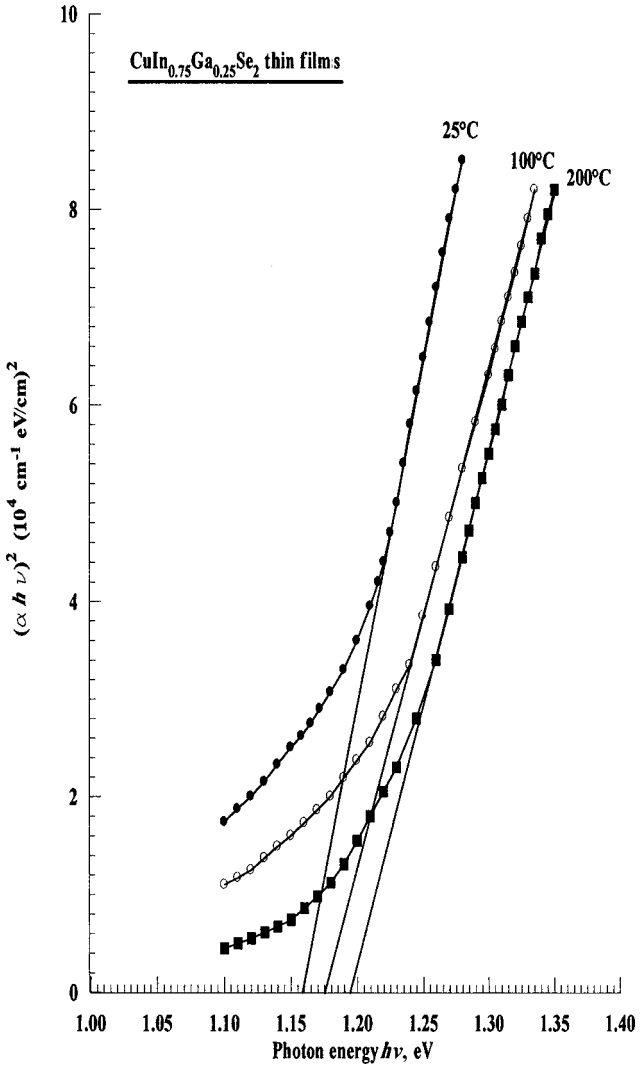

Fig. 7 Room temperature plots of $(\alpha h\nu)^2$ versus photon energy of polycrystalline CIGS films

In determining the respective energy band gap values of the flash-evaporated CIGS thin film samples, $(\alpha h\nu)^2$ was plotted against the photon energy. Figure 7 shows the representative curves obtained. Extrapolation of the curves down to a zero $(\alpha h\nu)^2$ level gave an energy value of 1.159 eV for the film deposited at room temperature. This band gap value increased as the substrate temperature was raised. The resultant shift was 1.175 eV for 100 °C and 1.194 eV for 200 °C. The band gap value of 1.194 eV for films deposited at 200 °C substrate temperature is in good agreement with the reported value (Ref 5, 11). The low band gap value for the film deposited at room temperature appears to be linked to structural imperfections. The films deposited by such methods contain additional states in the vicinity of the band edge caused by structural defects within the grains and grain boundaries, causing a smaller effective band edge. This behavior is consistent with results from scanning electron microscopy, XRD, and Raman spectra (Ref 9).

4. Conclusions

Photoacoustic spectrometry in transmission mode can produce identical results to those obtained using the standard photoacoustic system or spectrophotometer, but the analysis of the data from thin film samples is greatly simplified. An added advantage of this new configuration is its ease of operation. In the standard setup, each new sample has to be resealed before spectra can be obtained. In transmission mode, the cell is initially filled with carbon black and then sealed for life. Each new sample, regardless of its size, is simply placed on top of the photoacoustic cell quartz window and the spectra obtained. The calculated energy band gap values of flash-evaporated CIGS thin films were found to be in good agreement with each other as well as to those reported in the literature.

References

1. K. Ramanathan, M.A. Contreras, C.L. Perkins, S. Asher, F.S. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Noufi, et al., Properties of 19.2% Efficiency ZnO/CdS/CuInGaSe$_2$ Thin-Film Solar Cells, *Prog. Photovolt.,* 2003, **11,** p 225-230
2. J. Manifacier, J. Gasiot, and J. Fillard, A Simple Method for the Determination of Optical Constants n, k, and the Thickness of Weakley Absorbing Thin Film, *J. Phys E: Sci. Instr.,* 1976, **9,** p 1002-1004
3. R. Swanepoel, Determination of Surface Roughness and Optical Constants of Inhomogeneous Amorphous Silicon Films, *J. Phys. E: Sci. Instr.,* 1984, **17,** p 896-903
4. A. Rosencwaig, Ed., *Photoacoustic & Photoacoustic Spectroscopy*, John Wiley & Sons, New York 1980
5. E. Ahmed A. Zegadi, A.E. Hill, R.D. Pilkington, and R.D. Tomlinson, Optical Properties of Flash Evaporated CuIn$_{0.75}$Ga$_{0.25}$Se$_2$ Thin Films, *Thin Solid Films,* 1995, **268,** p 144-151
6. E. Ahmed, A.E. Hill, R.D. Pilkington, and R.D. Tomlinson, Growth and Annealing of CuIn$_{0.75}$Ga$_{0.25}$Se$_2$ Thin Films, *J. Phys. D: Appl. Phys.,* 1993, **26,** p 1787-1792
7. E. Ahmed, "Growth and Characterization of Cu(In,Ga)Se$_2$ Thin Films for Solar Cell Applications," Ph.D. thesis, University of Salford, U.K. 1995
8. I.E. Elfallal, "ITO Thins Films Using E-Beam Evaporation," Ph.D. thesis, University of Salford, U.K. 1993
9. E. Ahmed, A. Zegadi, A.E. Hill, R.D. Pilkington, and R.D. Tomlinson, The Influence of Annealing Processes on the Structural, Compositional and Electro-Optical Properties of CuIn$_{0.75}$Ga$_{0.25}$Se$_2$ Thin Films, *J. Mater. Sci.: Mater. Electron.,* 1996, **7,** p 213-219
10. E. Ahmed, A. Zegadi, A.E. Hill, R.D. Pilkington, R.D. Tomlinson, and W. Ahmed, "Thermal Annealing of Flash Evaporated Cu(In,Ga)Se$_2$ Thin Films, *J. Mater. Process. Technol.,* 1998, **77,** p 260-265
11. A. Zegadi, M.A. Slifkin, M. Djamin, R.D. Tomlinson, and H. Neumann, Photoacoustic Spectroscopy of Defect States in CuInSe$_2$ Single Crystals, *Solid State Commun.,* 1992, **83,** p 587-591
12. K.L. Chopra, Ed., *Thin Film Phenomena,* Krieger, New York, 1979