The impact of Se-content on the optical properties of $CuInSe_2$ by using transmittance and photoacoustic spectroscopies

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Abstract

In this paper, we present the results obtained from measurements of $CuInSe_2$ single crystals in which we varied the selenium content prior to the growth from -2% to +5% using two different optical characterization techniques, transmittance and photoacoustic. The results obtained from the two techniques are compared in the light of recent published data.

Key words: $CuInSe_2$, optical properties, photoacoustic spectroscopy, transmittance, defects

1. Introduction

Despite their polycrystalline nature, thin-film solar cells based on the chalcopyrite compounds of $CuInSe_2$ (CIS) and its alloys $Cu(In,Ga)Se_2$ (CIGS) achieve surprisingly high conversion efficiencies in excess of 20% [1]. Yet, this value is still distinctly below that of 25% predicted theoretically. This is due to a lack of understanding of the complex defect structure of these compounds [2-3]. Numerous experimental investigations have shown that the electrical properties of the compound are dominated by various types of electrically active intrinsic defects associated with deviations from stoichiometry [4].

Photoacoustic spectroscopy has emerged recently as a promising technique for investigating the optoelectronic properties of semiconductors. One of its main advantages, apart from being non-destructive and contactless, it is virtually unique in observing non-radiative defect populations in semiconductors; these are known to be associated with energy loss mechanisms in devices [5], [6].

In this paper, using the transmittance and photoacoustic techniques we investigate the impact in changing the selenium content prior to the growth of $CuInSe_2$ single crystals on the defect structure of this compound. Many defect levels have been attributed to Se-related defects, and different interpretations are reported in the literature [7]. Absorption coefficients have been derived from the photoacoustic and transmittance spectra to establish activation energies for several defect-related energy levels.

2. Experimental

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The samples used in this work were grown by the vertical Bridgman technique from melts with different selenium contents. These were varied from the stoichiometric value by approximately 5%. The actual measured Se compositions are established during the growth since the compound does not freeze congruently.
High quality, crack-free samples are used in the experiments. The composition of the samples as determined by electron microprobe measurements is given in Table 1.

Table 1. Data related to the samples used in this work.

Sample	Thickness (μm)	Cond. type	Init. Se-Content	Composition		
				[Cu] atm. %	[In] atm. %	[Se] atm. %
C-1	200	n	- 5%	23.5	26.19	50.31
C-2	200	p	Stoichiom.	23.23	26.59	50.18
C-3	200	p	+ 2%	23.29	26.09	50.02
C-4	200	p	+ 5%	22.42	26.52	51.06

Apart from the last sample which has been grown with an excess of Se that shows an amount of this latter above the stoichiometric composition, the other samples showed a near stoichiometric composition. All samples showed a deficiency in Cu contents and as a result the defect “vacancy in Cu” will play an important role in defect structure that can be detected.
It has been found that single crystals with compositions in this range can be both p-type and n-type conducting [8-9] in dependence on the specific intrinsic defect equilibrium.
Prior to any measurement the samples were mechanically polished on both sides (the final stage employed a vibratory polisher with Al_2O_3 powder of particle size 0.05μm) and subsequently etched for a minute in a 1% bromine in methanol solution.
The photoacoustic spectrometer has been described in detail elsewhere [6]. Measured photoacoustic spectra are corrected for the spectral distribution of the optical system, the microphone, and the cell by normalizing the response of the specimens to that of fine particles of carbon black. All spectra were obtained at room temperature at the modulating frequency of 112 Hz. As for the transmittance spectrometer, we have used a standard UV/Visible/Infrared one.

3. Results and discussion

Figure 1 depicts the transmittance spectra measured at room temperature as a function of the photon energy hν from the samples of $CuInSe_2$ single crystal in the photon energy range 0.7 eV ≤ hν ≤ 1.2 eV. We note the shift to the fundamental edge with varying contents of Se.
Figure 2 shows the photoacoustic spectra measured at room temperature from the samples. Also shown in the figure, as indicated by an arrow, is the bandgap (E_g = 1.01 eV) as reported in the literature. We should notice that this coincides well with the upper limit of the normalized amplitude of the PA signal. Three distinct spectral regions are observed:

- The transparency region, Region 1: where hν ≤ 0.92 eV, the samples is nearly transparent and peaks that are observed here can be associated with transitions between non-radiative defect

states and the conduction/valence bands. In this spectral region the PA signal is generated as a result of the heat that arises within the sample thermal diffusion length (μ_s).

- The fundamental edge region, Region 2: 0.92 eV ≤ hν ≤ 1.05 eV, the spectra clearly show the direct nature band to band transition edge. A clear difference in the curves up rise of the amplitude of the PA signal is observed. This is a characteristic of a shallow defect level.
- The saturation region, at hν ≥ 1.05 eV, all the incident light beam is absorbed within a thin layer of thickness in the order of the optical diffusion length. This region gives information on the surface state as determined by the reflection effect [6].

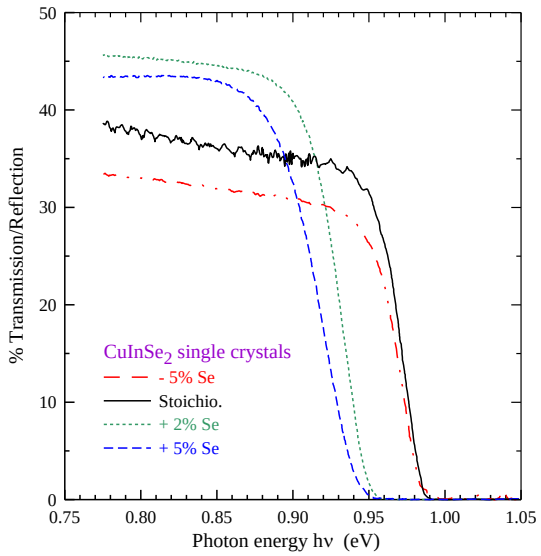

Figure 1. Transmittance spectra measured of the samples used in this work.

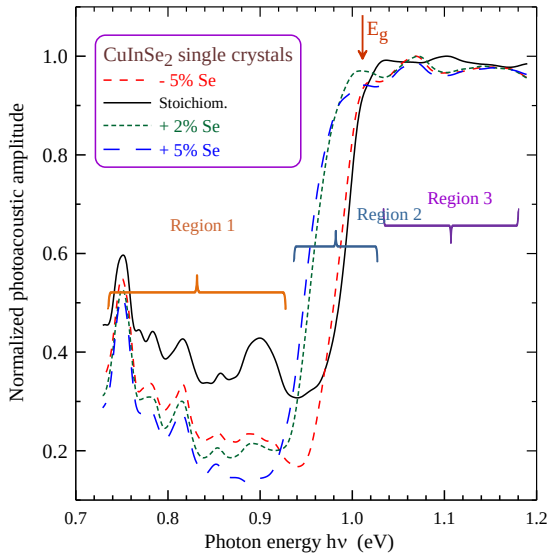

Figure 2. Photoacoustic spectra measured of the samples used in this work.

The shift in the fundamental edge by the transmittance technique is also observed from photoacoustic spectra. However, the latter contains more information that the spectra measured by the transmittance technique. The fundamental edge observed from C-1 and C-2 is almost the same, and that's from both techniques.

In deriving the absorption coefficient spectrum from measured photoacoustic spectra, Neumann [10] indicated for the case where the normalized photoacoustic amplitude (q) is less or equal to 0.2, the multiple reflections of the incident radiation within the sample interfaces have to be taken into account. At values $q \geq 0.2$, this effect is negligible. It follows that the functional dependence of the absorption coefficient on the PA amplitude signal (q) is given by the relation:

$$\alpha = \frac{1}{\mu_s} \frac{q^2 + q\sqrt{2 - q^2}}{1 - q^2} \tag{1}$$

This applies to all our samples apart from the sample C-4, in which the multiple reflections at the sample interfaces has to be taken into consideration.

Fig. 3 shows, for instance, the absorption coefficient spectra which were derived directly from the normalized PA amplitude data near the fundamental edge of the samples of Figure 2. In this spectral region, we should notice the presence of a shoulder displayed with respect to part of the spectrum of the sample grown with near stoichiometric composition (C-2) and is characteristic of a shallow defect level.

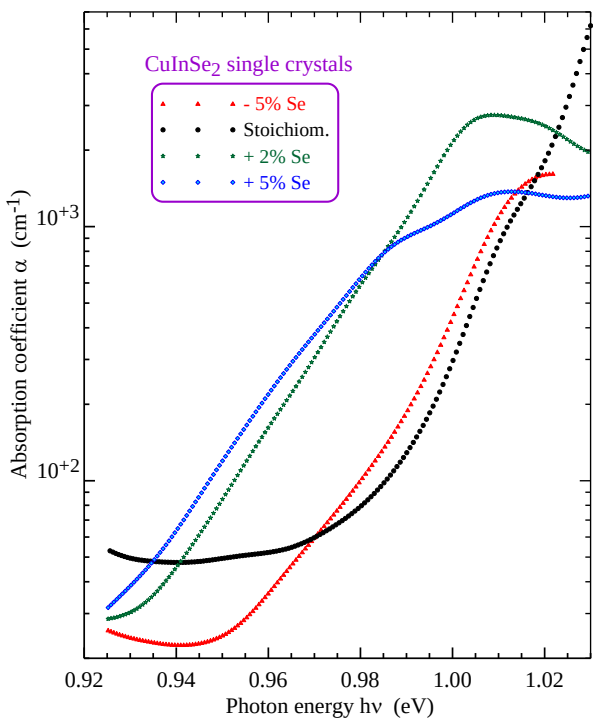

Figure 3. Absorption coefficient derived from PA spectra.

As Se-content is increased as the shoulder occupies larger area of the spectrum. As for the

sections of the photoacoustic spectra below the energy gap for the samples, shown in Figure 4, five major peaks are resolved in the absorption spectra with varying intensities due to differing defect concentrations. These are associated with transitions between non-radiative defect states and the conduction/valence bands. These defect states have been discussed in detail in our early work [6].

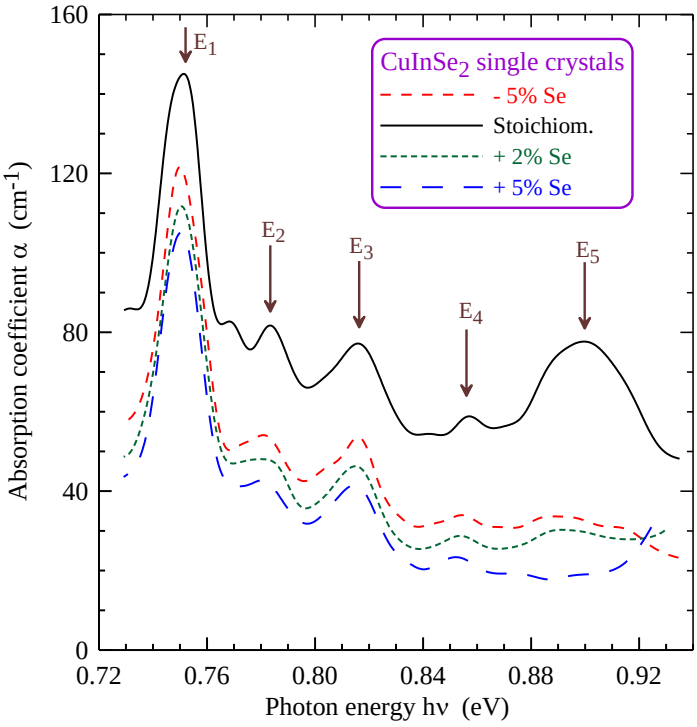

Figure 4. Comparative plot of absorption coefficients showing deeper transitions.

The defect level E5 seems the mostly affected by the selenium content. In the literature, this level has been assigned to both donor and acceptor states and no definite attribution has made so far.

Conclusion

Summarizing the results of the present study on $CuInSe_2$ we come to the following conclusions: photoacoustic spectroscopy revealed the presence of several peaks in the region of weak absorption. Photoacoustic is shown to be more sensitive to Se-content than the transmittance technique. Defects have been detected which are associated with shallow and deep levels and which are influenced by the selenium content of the samples. It has been shown that there are more than two defect levels that are due to Se contrarily to what it has been reported in the literature.

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