Optical Properties of High Quality Cu$_2$ZnSnSe$_4$ Thin Films

F.Luckert[1], D. I. Hamilton[1], M.V.Yakushev[1], A.V.Karotki[3], A.V.Mudryi[1,3], M. Grossberg[4], J.Krustok[4] N.Beattie[2], G.Zoppi[2], M. Moynihan[2], I. Forbes[2] and R.W. Martin[1]

[1] *Department of Physics, SUPA, Strathclyde University, G4 0NG Glasgow, UK,*
franziska.luckert@strath.ac.uk
[2] *Northumbria Photovoltaics Applications Centre, Northumbria University, Ellison Building,*
Newcastle upon Tyne NE1 8ST, UK
[3] *Scientific-Practical Material Research Centre of the National Academy of Science of Belarus,*
P.Brovki 19, 220072 Minsk, Belarus
[4] *Tallinn University Technology, Ehitajate tee 5, Tallinn 19086, Estonia*

Introduction

The increasing cost and limited availability of indium, one of the main components in CuInSe$_2$-based thin film solar cells, has resulted in a growing interest in the related semiconductor compounds Cu$_2$ZnSn(S,Se)$_4$ whose crystalline structure is similar to chalcopyrite with In substituted by alternating zinc (Zn) and tin (Sn). The possibility of p-type doping by intrinsic defects and a high absorption coefficient, exceeding 10^4 cm^{-1}, in the visible range [1], make this new compound attractive for the application as an absorber layer in thin film solar cells. The recently reported conversion efficiency record of 9.6% [2] demonstrates a high potential and make this compound, which contains neither expensive nor hazardous atomic species, a strong competitor to the chalcopyrite Cu(In,Ga)Se$_2$ as an absorber layer material for the large-scale production of thin-film solar cells.

Reliable knowledge of the essential fundamental electronic properties can significantly accelerate the development process of photovoltaic (PV) electronic devices. The most efficient technique for gaining such knowledge is optical spectroscopy [3-5]. However, the usefulness of such methods depends critically on the availability of high quality material, with sharp and well-resolved spectral features required for elucidation of the desired information. Despite the high record efficiency the structural quality achieved thus far in Cu$_2$ZnSn(S,Se)$_4$ material is generally rather low: in the majority of publications the photoluminescence (PL) spectra reveal only one broad, low intensity band ascribed to radiative recombination of free electrons and holes localised at shallow acceptors [6]. The width of this band and its asymmetric shape suggest high concentrations of defects and the influence of band tails induced by randomly distributed charged defects. Very little information on fundamental properties can be gained from the optical spectra of such material. As a result one of the most important parameters for design of electronic devices, namely the band gap energy, has been the subject of controversy with values for Cu$_2$ZnSnSe$_4$ (CZTSe) varying from 0.86 [7] to 1.62 eV [8] in different publications.

In this report we demonstrate the possibility to fabricate excitonic grade CZTSe thin films, revealing phonon replicae of a donor-acceptor pair (DAP) recombination in the PL spectra. This provides an experimental value for the longitudinal optical (LO) phonon energy and the band gap energy is clarified using optical absorption (OA) spectra.

Experimental Details

Thin films of CZTSe were fabricated by magnetron sputter deposition of Cu, Zn and Sn precursor layers from high-purity (5N) elemental targets. Both Mo-coated and bare soda-lime glass substrates were used at room temperatures and the precursor layers selenised at temperatures of 530°C for 15 min in an atmosphere containing a mixture of Ar and Se vapour.

The morphology and elemental composition of the films were studied by scanning electron microscopy (SEM) combined with wavelength dispersive X-ray (WDX) microanalysis using a Cameca SX100. The structural properties of the films and the presence of secondary phases were studied by x-ray diffraction (XRD) using a Siemens D5000 diffractometer as well as by Raman spectroscopy employing a Horiba`s LabRam HR spectrometer with a multichannel CCD in a backscattering configuration. The incident light beam of a 532 nm wavelength laser was focused to a 10 μm diameter spot on the samples.

Opto-electronic properties of the films were examined by photoluminescence (PL) at temperatures from 4.2 to 300 K using a closed cycle cryostat and the 514 nm line of a 100 mW Ar$^+$ laser for excitation. A 1 m monochromator with a 600 grooves/mm grating was used and the detector was a cooled InGaAs photomultiplier tube (Hamamatsu H9170-75). Optical transmission and reflection measurements were performed at room temperature in the spectral range from 600 – 1800 nm using a Cary 500 Scan UV-Vis-NIR spectrophotometer (Varian, USA).

Results & Discussion

The cross-section of a film deposited on bare glass, shown in Fig.1(a), reveals a dense homogeneous film with an average thickness of 700 nm. A quantitative WDX elemental composition line-scan, shown in Fig.1(b), demonstrates good lateral homogeneity of the films. The ratios of the elements are [Cu] / [Zn+Sn] = 1.05 ± 0.02, [Se] / [Cu+Zn+Sn] = 0.91 ± 0.01 and [Zn]/[Sn] = 0.94 ± 0.03, suggesting a small excess of copper as well as a deficiency of zinc and selenium.
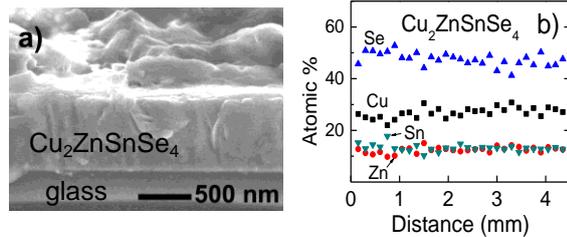
Figure 1 a) Cross sectional SEM micrograph of a CZTSe film on glass, b) WDX linescan.

Fig 2(a) shows the XRD spectrum of the CZTSe film on Mo on a logarithmic scale to highlight possible low intensity peaks. The spectrum reveals several distinct CZTSe peaks, a strong molybdenum peak and two low intensity MoSe$_2$ peaks. These peaks imply that the selenisation reaction has continued through the precursor layer reaching the molybdenum substrate.

In the room temperature Raman spectra of the films on bare glass and Mo, shown in Fig. 2(b), the modes at 169, 173 cm^{-1}, 196.6 and 234 cm^{-1}, as reported earlier [6] and assigned to CZTSe, can be seen. The Cu$_x$Se mode at 261 cm^{-1} can also be found at a few small spots randomly distributed across the surface. However, the main part of the surface was found to be free from secondary phases. The 242 cm^{-1} Raman line associated with MoSe$_2$ has rather low intensity when measured at the top of a dense, homogeneous film. Its intensity increases significantly when the laser beam is focused closer to the Mo layer suggesting that the MoSe$_2$ phase is present mainly at the Mo/CZTSe interface. The formation of the MoSe$_2$ phase has also been reported at the Mo/CZTSe interface after selenisation at 500° C [9]. None of the other secondary phases reported in [6] were observed in the Raman spectra of the CZTSe thin film.

The full width at half maximum (FWHM) of the dominant A$_1$ mode is 3 cm^{-1}. This is significantly smaller than the 10 cm^{-1} estimated in the Raman spectrum reported by Ahn et al. [9] and suggests superior structural quality for our material.

In order to clarify the band gap energy room temperature optical absorption $\alpha(h\nu)$ has been calculated using both optical transmission and reflection data [10]. For an allowed direct transition

the spectral dependence of the absorption coefficient can be calculated as follows [11]

$$\alpha = \frac{A}{h\nu}(h\nu - E_g)^{1/2} \qquad (1)$$

with A a constant, E_g the optical band gap energy.
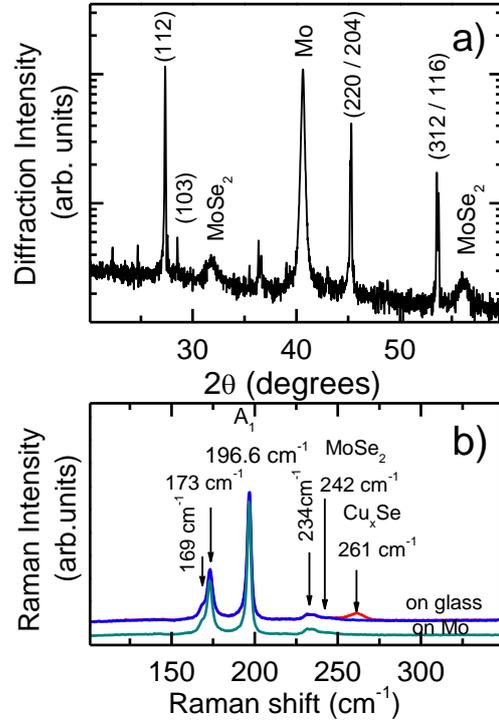
Figure 2 a) XRD pattern of a CZTSe film on Mo, b) Raman spectra of the CZTSe thin films on glass and Mo.

Figure 3 plots the room temperature dependence of $(\alpha h\nu)^2$ on $h\nu$. energy axis, resulting in a band gap energy of E_g = 1.01 eV at room temperature.

This value is in good agreement with the those determined experimentally by Ahn et al. [9] and Grossberg et al. [6] as well as theoretically by Chen et al. [12]. Fig. 4(a) shows the evolution of the near band edge PL spectra with excitation intensity. The spectra are dominated by a relatively narrow PL band at 0.989 eV (DAP) and two lower intensity bands at 0.963 eV (DAP$_{1LO}$) and 0.932 eV (DAP$_{2LO}$). In order to determine the spectral positions and integrated intensity the experimental data points of the DAP, DAP$_{1LO}$ and DAP$_{2LO}$ have been fitted by three Gaussians. Figs. 4(b) and (c) show the dependencies of the integrated intensity (I) and the spectral position of the DAP peak on the excitation power, respectively. The integrated PL intensity of the DAP band increases as $I \sim P^\gamma$, where P is the excitation power. The linear fit in Fig. 3(b) gives a γ power coefficient of $\sim$ 0.63, as expected for defect related transitions [13]. The optical band gap E_g of the CZTSe films has been determined by extrapolating the linear part of the $(\alpha h\nu)^2$ dependence to the phonon The small blue shift with increasing excitation power, at a rate of 2.9

meV/decade, confirms that the peak involves recombination of a donor-acceptor pair (DAP) [14].
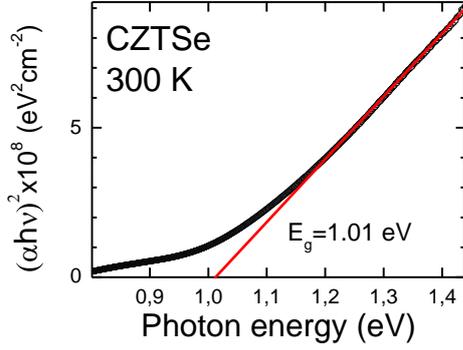
Figure 3 Optical absorption spectrum of CZTSe calculated at room temperature.

The spectral position of the band maximum of the $h\nu_{max}$ DAP recombination can be found as:

$$h\upsilon_{\max} = E_g - (E_d + E_a) + \frac{e^2}{\varepsilon r}$$

$$(2)$$

where E_d and E_a are the donor and acceptor ionisation energies, respectively, r is the spectral distance between the donor and acceptor levels in the band gap, e is the electron charge and ε is the static dielectric constant. The last term of equation 2 describes the Coulomb interaction between the donor and acceptor like defects. As the excitation power increases the concentration of occupied donor and acceptor centres increases whereas the average distance between these defects decreases resulting in a higher Coulomb interaction energy and a shift toward of the band towards higher energy.

The spectral position of the two lower intensity bands DAP_{1LO} and DAP_{2LO} also shift towards higher energies with increasing excitation power at the same rate as the DAP band (2.9 meV/decade). The spectral distance between the DAP and the DAP_{1LO} bands as well as between the DAP_{1LO} and DAP_{2LO} bands is about ~ 28 meV, which is close to the LO phonon energy in the CZTSe related chalcopyrite component $CuInSe_2$ [15]. Therefore DAP_{1LO} and DAP_{2LO} can be assigned to phonon-assisted DAP recombination with a LO phonon energy of $E_{LO} = 28$ meV. To the best of our knowledge this is the first experimental measurement of the LO phonon energy in CZTSe.

The PL spectra, shown in Fig.4 (a), also reveal a high-energy feature EX at ~ 1.033 eV. This feature can better be seen at higher excitation intensities and, as shown in Figure 5, does not exhibit any shift with varying excitation power.

The spectral position and the excitation power dependent behaviour of the EX feature suggests that this band can be attributed to a recombination of free excitons.
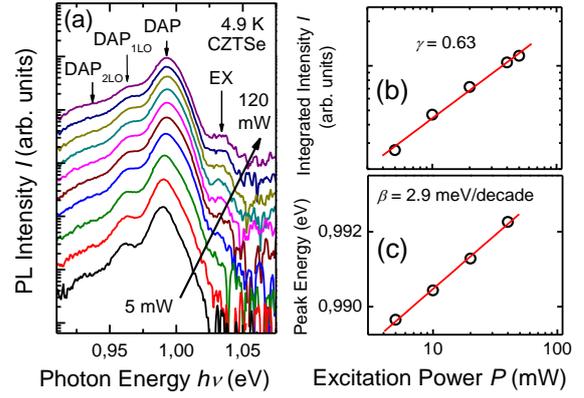
Figure 4 a) Excitation power dependence of the CZTSe PL spectra taken at 4.9 K, b) log/log dependence of the integrated intensity I on the excitation power P, c) dependence of the spectral position of the DAP peak on on log(P).

Although excitonic luminescence in the related chalcogenide component Cu_2ZnSnS_4 has been reported by Hones et al. [16] no excitonic luminescence has so far been reported in CZTSe due to the low quality of the material. The evolution of the PL spectra with temperature increasing from 5 to 60 K is shown in figure 6.
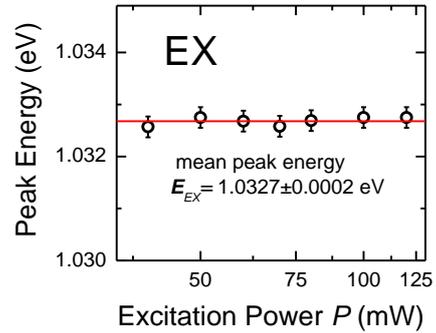
Figure 5 Dependence of the EX peak position on the excitation power.

With increasing temperature the intensity of all PL bands decreases. The temperature quenching is due to the thermally activated level depopulation or/and to the activation of a non-radiative recombination centre. An Arrhenius plot can be used to determine activation energies E_a of the process. The exciton peak is quenching at around 13 K which makes it impossible to determine an activation energy. The width and the quenching character of this feature suggest that it contains several non-resolved free and bound excitons.

The excitonic feature has been observed at liquid helium temperature whereas the band gap measurements were carried out at room temperature therefore we can not estimate the binding energy of the exciton.
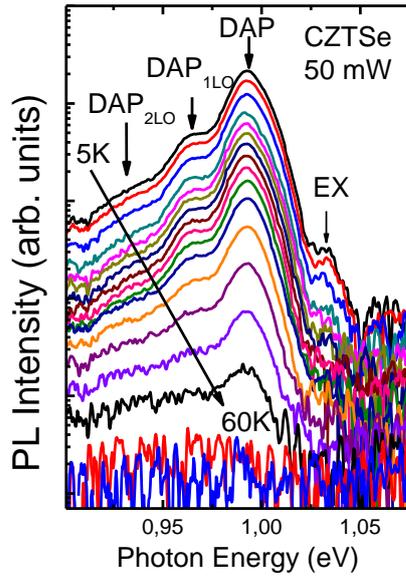
Figure 6 Temperature dependence of the PL spectra of the CZTSe film.

However, it is clear that the low temperature band gap energy should be quite close to the energy of the excitonic peak at 1.033 eV. The quenching dependence of the integrated PL intensity of the DAP band is shown in figure 7.
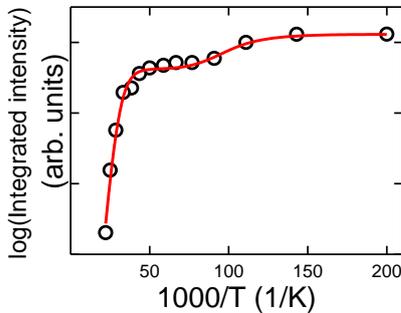
Figure 7 Temperature dependent quenching of the integrated intensity of the DAP peak.

A good fit of the experimental data points has been achieved assuming two independent recombination channels [17]:

$$I(T) = \frac{I_{01}}{1 + A_1 \exp\left(-E_{a1}/kT\right)} + \frac{I_{02}}{1 + A_2 \exp\left(-E_{a2}/kT\right)} \quad (3)$$

where I_0 (intensity at zero temperature), E_a (activation energies) and A are fitting parameters, and k is the Boltzmann constant. The determined activation energies of about $E_{a1} = 9$ meV and $E_{a2} = 23$ meV, suggest that the DAP includes two acceptors: a shallow at 9 meV and a deeper at 23 meV as suggested for Cu_2ZnSnS_4 by Hones et al.

[17]. More detailed analysis will be reported elsewhere.

Conclusion:

In conclusion, CZTSe thin films have been studied by WDX, XRD, Raman, OA and PL. The XRD and Raman demonstrated high structural quality of the material. The band gap value, established by optical absorption analysis, was found to be close to 1 eV at room temperature. The temperature quenching analysis of the PL spectra, dominated by a high-intensity and relatively narrow DAP band suggest that the DAP includes two acceptors at 9 and 23 meV above the valence band. For the first time phonon replicas of the DAP band and an excitonic feature have been observed in CZTSe. A LO phonon energy of ~ 28 meV was determined.

References:

1. Ito, K. and T. Nakazawa, Jpn. J. Appl. Phys., **27**(1988) 2094.
2. Todorov, T.K., et al., Advanced Materials, **22** (2010) 1.
3. M.V.Yakushev, A.V.Mudryi, I.V.Victorov, et al. Appl. Phys. Lett. 88, 011922 (2006).
4. M. V. Yakushev, F. Luckert, C. Faugeras, A. V. Karotki, A. V. Mudryi,and R. W. Martin, Appl.Phys. Lett. 97, 152110 (2010)
5. F. Luckert, M. V. Yakushev, C. Faugeras, A. V. Karotki, A. V. Mudryi, and R. W. Appl.Phys. Lett. 97, 162101 (2010)
6. Grossberg, M., et al., Thin Solid Films, **517** (2009) 2489.
7. Altosaar, M., et al., Physica Status Solidi a, **205** (2008) 167.
8. Babu, G.S., et al., Sol. Energy Mater. Sol. Cells, **94** (2010) 221.
9. Ahn, S., et al., Appl. Phys. Lett., **97** (2010) 021905.
10. A.V.Mudryi, V.F.Gremenok, I.A.Victorov, et al. Thin Solid Films, 431/432, **2003**, p.193
11. Pankove, J.I., Optical Processes in Semiconductors. 1975, Dover Publications
12. Chen, S.Y., et al., Appl. Phys. Lett., **94** (2009) 041903.
13. Schmidt, T., et al., Phys. Rev. B,. **45** (1992) 8989.
14. Dingle, R., Phys. Rev., **184**(1969) 788.
15. Tanino H., et al., Phys.Rev.B., **45** (1992) 13323.
16. Hones, K., et al.,. Physica B, **404** (2009) 4949.
17. J. Krustok, H. Collan and K. Hjelt J.Appl. Phys. 81 (1997) 1442.