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Optical Properties of High Quality $Cu_2ZnSnSe_4$ Thin Films

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$Cu_2ZnSnSe_4$ thin films, fabricated on bare or molybdenum coated glass substrates by magnetron sputtering and selenisation, were studied by a range of techniques. Photoluminescence spectra, revealing an excitonic peak and two phonon replicas of a donor-acceptor pair (DAP) recombination, demonstrate the possibility to fabricate high quality $Cu_2ZnSnSe_4$ thin films and provide with experimental value of 28 meV for the longitudinal optical (LO) phonon energy. The DAP recombination includes two acceptors and a donor with ionisation energies of 12, 27 and 7 meV, respectively. The band gap energy of 1.01 eV at room temperature is clarified using optical absorption spectra.

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 $Cu_2ZnSn(S,Se)_4$ 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, containing neither expensive nor hazardous atomic species, a 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 resolved features in the optical spectra. Despite the high record efficiency the structural quality currently achieved in $Cu_2ZnSn(S,Se)_4$ is 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 the influence of band tails induced by randomly distributed high concentrations of charged defects. Very little information on fundamental properties can be gained from the optical spectra of such material. As a result the band gap energy for $Cu_2ZnSnSe_4$ (CZTSe), one of the most important parameters for design of electronic devices, is the subject of controversy varying from 0.8 [7] to 1.62 eV [8].

In this report we demonstrate the possibility to fabricate excitonic grade CZTSe thin films, with PL spectra revealing an exciton peak as well as phonon replicas of a donor-acceptor pair (DAP) recombination providing an experimental value for the longitudinal optical (LO) phonon energy. The band gap energy is clarified using optical absorption (OA) spectra.

Thin films of CZTSe were fabricated by magnetron sputter deposition of Cu, Zn and Sn precursor layers from high-purity (5N) elemental targets on unheated either Mo-coated or bare soda-lime glass substrates and then selenised at temperatures of 530°C for 15 min in 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. The structural properties of the films and the presence of secondary phases were studied by X-ray diffraction (XRD) as well as by Raman spectroscopy. 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 was employed to analyse opto-electronic properties. Optical transmission and reflection measurements were performed at room temperature in the spectral range from $600 - 1800$ nm to establish the band gap value.

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 $\pm$ 0.02, [Se] / [Cu+Zn+Sn] = 0.91 $\pm$ 0.01 and [Zn]/[Sn] = 0.94 $\pm$ 0.03, suggesting a small excess of copper as well as a deficiency of zinc and selenium.

Fig 1(c) 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. 1(d), 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_xSe 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.
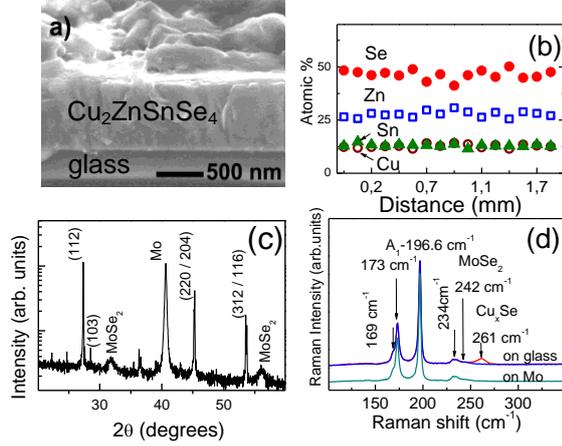

FIG. 1. a) Cross sectional SEM micrograph of a CZTSe film on glass, b) WDX linescan, c) XRD pattern of a CZTSe film on Mo, d) Raman spectra of the CZTSe thin films on glass and Mo.

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 (not shown here) 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 [11] $\alpha = A(h\nu - E_g)^{1/2} / h\nu$ with constant A and optical band gap energy E_g. Fig. 3(a) plots a room temperature dependence of $(\alpha h\nu)^2$ on photon energy $h\nu$. The optical band gap of $E_g = 1.01$ eV has been determined by extrapolating the linear part of the $(\alpha h\nu)^2$ dependence to the photon energy axis. 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. 2(b) shows the evolution of the near band edge PL spectra with changing excitation intensity. At 4.5 K the PL spectra are dominated by a relatively narrow PL band at 0.989 eV (DAP) and the two lower intensity bands at 0.963 eV (DAP$_{1LO}$) and 0.932 eV (DAP$_{2LO}$). In order to determine their spectral positions and integrated

intensity the experimental data points of the DAP, DAP$_{1LO}$ and DAP$_{2LO}$ have been fitted by three Gaussians. A small blue shift at a rate of 2.9 meV/decade with increasing excitation power, suggests that the peak originates from a donor-acceptor pair (DAP) recombination [14].

The integrated PL intensity of the DAP band increases with excitation power P growth as $I \sim P^\gamma$, where power coefficient $\gamma \approx 0.63$ suggesting that this band is a defect related transitions [13].
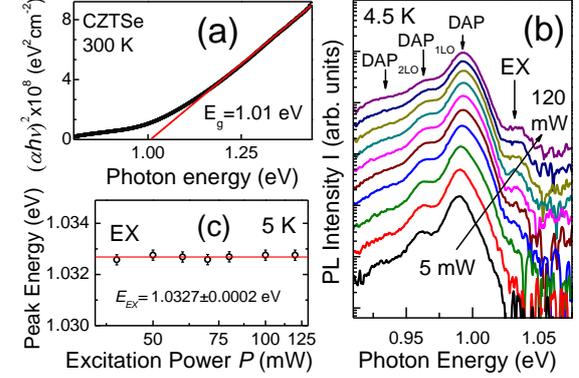

FIG. 2. Room temperature dependence of $(\alpha h\nu)^2$ on photon energy $h\nu$ (a), evolution of the PL spectrum with increasing excitation power P (b), excitation power dependence of the EX peak at 5 K (c).

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

$$h\nu_{max} = E_g - (E_d + E_a) + \frac{e^2}{\varepsilon r}, \qquad (1)$$

where E_d and E_a are the donor and acceptor ionisation energies, respectively, r is the distance between the donor and acceptor, e is the electron charge and ε is the static dielectric constant. The last term of (1) describes the Coulomb interaction between the donor and acceptor like defects. As the excitation power increases the concentration of occupied donor and acceptor centres also increases reducing the average distance between these defects resulting in a higher Coulomb interaction energy and a shift of the band towards higher energy.

The spectral positions 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 chalcopyrite $CuInSe_2$ [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.

The PL spectra, shown in Fig.2 (b), 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 Fig. 2(c), does not exhibit any shift at 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 excitons. Excitonic luminescence in the related chalcogenide component Cu_2ZnSnS_4 has been reported by Hones et al. [16]. However 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 Fig. 3(a). The intensity of all PL bands decreases. This temperature quenching is due to the thermally activated depopulation of the defect energy levels 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 value. The width and the quenching character of this feature suggest that it contains non-resolved free and bound excitons.
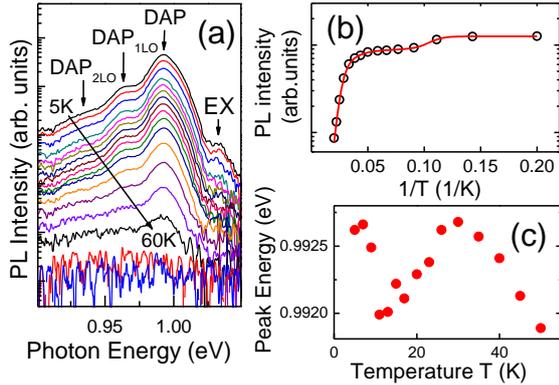

FIG.3. Temperature dependence of the PL spectra (a), temperature quenching of the integrated intensity of the DAP peak (○ - experimental points, - fitted line) (b), dependence of the DAP peak spectral position on temperature (c).

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. 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 same low temperature band gap energy was recently confirmed by the temperature dependence of quantum efficiency spectra of CZTSe solar cells [17].

The temperature quenching dependence of the integrated PL intensity of the DAP band is shown in Fig. 3(b). It shows two distinct regions: below and above 10 K. The best fit of the experimental data points has been achieved assuming three recombination channels [18]:

$$(2)$$
$$I(T) = \frac{I_{01}}{1 + A_1 \exp\left(-\dfrac{E_{a1}}{kT}\right)} + \frac{I_{02}}{1 + A_2 \exp\left(-\dfrac{E_{a2}}{kT}\right) + A_3 \exp\left(-\dfrac{E_{a3}}{kT}\right)}$$

where I_0 (intensities at the lowest temperature), E_a (activation energies) and A are fitting parameters (k is the Boltzmann constant). The determined activation energies are $E_{a1} = 13 \pm 2$ meV, $E_{a2} = 27 \pm 3$ meV and $E_{a3} = 7 \pm 2$ meV. These values are very close to those determined in the related compound Cu_2ZnSnS_4 by Hones et al. [16]. We propose a similar model of recombination including two acceptor and one donor. The low temperature quenching is described by the first term of (2) and associated with a shallower acceptor with the energy level 13 meV above the valence band. Ionisation of this acceptor results in a lower energy shift of the DAP peak as shown in Fig.3(c). At temperatures increasing above 10 K the DAP peak is becoming narrower and gradually

shifting to the higher energy because ionisation of the donor with the energy level 7 meV below the conduction band transforms the DAP recombination into a recombination of electron from the conduction band and hole localised at the deeper acceptor with the energy level 27 meV above the valence band.

In conclusion, CZTSe thin films have been studied by WDX, XRD, Raman, OA and temperature resolved PL. The XRD and Raman spectra demonstrate high structural quality of the material. The band gap value, established by optical absorption analysis at room temperature, was found to be close to 1 eV. The temperature quenching analysis of the dominating high-intensity and relatively narrow DAP band suggests that this band includes two acceptors at 13 and 27 meV above the valence band, and a donor at 7 meV below the conduction band. Two phonon replicas of the DAP band and an excitonic feature have been observed in the PL spectra. An experimental LO phonon energy of ~ 28 meV was determined.

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