Optical properties of high quality \( \text{Cu}_2\text{ZnSnSe}_4 \) thin films


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\( \text{Cu}_2\text{ZnSnSe}_4 \) thin films, fabricated on bare or molybdenum coated glass substrates by magnetron sputtering and selenisation, were studied by a range of techniques. Photoluminescence spectra reveal an excitonic peak and two phonon replicas of a donor-acceptor pair (DAP) recombination. Its acceptor and donor ionisation energies are 27 and 7 meV, respectively. This demonstrates that high-quality \( \text{Cu}_2\text{ZnSnSe}_4 \) thin films can be fabricated. An experimental value for the longitudinal optical phonon energy of 28 meV was estimated. The band gap energy of 1.01 eV at room temperature was determined using optical absorption spectra. © 2011 American Institute of Physics. [doi:10.1063/1.3624827]

The increasing cost and limited availability of indium, one of the main components in \( \text{CuInSe}_2 \)-based thin film solar cells, have resulted in a growing interest in the related semiconductor compounds \( \text{Cu}_2\text{ZnSn(S,Se)}_4 \), whose crystalline structure is similar to chalcopyrite with In substituted by Sn. The possibility of p-type doping by intrinsic defects and a high absorption coefficient, exceeding \( 10^5 \text{ cm}^{-1} \), in the visible range makes 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% [Ref. 2] demonstrates a high potential of the material. As a result, values for the energy of the CZTSe band gap, which is one of the most important material parameters for design of electronic devices, are found to vary from 0.8 in Ref. 8 to 1.62 eV in Ref. 9. Ahn et al. have discussed differences relating to phases, not detected by x-ray diffraction (XRD), and concluded that the CZTSe band gap is close to 1 eV.\(^{10}\)

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 from high-purity (5N) elemental targets as layered precursors on unheated substrates of either Mo-coated or bare soda-lime glass as described previously.\(^{11}\) These precursors were 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 XRD as well as by Raman spectroscopy. 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 were 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 \( \text{Cu}/[\text{Zn} + \text{Sn}] = 1.05 \pm 0.02 \), \( \text{Se}/[\text{Cu} + \text{Zn} + \text{Sn}] = 0.91 \pm 0.01 \), and \( \text{Zn}/[\text{Sn}] = 0.94 \pm 0.03 \),
indicating a small excess of copper as well as a deficiency of zinc and selenium.

Figure 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 MoSe₂ 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, 196.6, and 234 cm⁻¹, as reported earlier in Ref. 6 and assigned to CZTSe, can be seen. The Cu₂⁻Se mode at 261 cm⁻¹, identified earlier,¹² 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 MoSe₂ 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 MoSe₂ phase is present mainly at the Mo/CZTSe interface. The formation of the MoSe₂ phase has also been reported in Ref. 10 at the Mo/CZTSe interface after selenisation at 500°C. None of the other secondary phases reported in Ref. 6 were observed in the Raman spectra of the CZTSe thin film.

The full width at half maximum (FWHM) of the dominant A₁ mode is 3 cm⁻¹. This is significantly smaller than the 10 cm⁻¹ estimated in the Raman spectrum, reported by Ahn et al.,¹⁰ and suggests superior structural quality for our material. In order to clarify the band gap energy, room temperature optical absorption α(ℏν) has been calculated using both optical transmission and reflection data.¹³ For an allowed direct transition, the spectral dependence of the absorption coefficient can be calculated as $α = A(ℏν - E_g)^{1/2}$ (Ref. 14) with constant $A$ and optical band gap energy $E_g$. Fig. 3(a) plots a room temperature dependence of $(αℏν)^2$ on photon energy $ℏν$. The optical band gap of $E_g = 1.01$ eV has been determined by extrapolating the linear part of the $(αℏν)^2$ dependence to the photon energy axis. This value is in good agreement with those determined experimentally by Ahn et al. in Ref. 10 and Grossberg et al. in Ref. 6 as well as theoretically by Chen et al.¹⁵

Figure 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 (DAP₁LO) and 0.932 eV (DAP₂LO). In order to determine their spectral positions and integrated intensity, the experimental data points of the DAP, DAP₁LO, and DAP₂LO 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 DAP peak originates from a donor-acceptor pair recombination.¹⁶

The integrated PL intensity of the DAP band increases with increasing excitation power $P$ as $I \sim P^c$, with the power coefficient $c = 0.63$, suggesting that this band is due to defect related transitions.¹⁷ The spectral position of the DAP band maximum $ℏν_{max}$ can be described as

$$ℏν_{max} = E_g - (E_d + E_a) + \frac{e^2}{4\pi\varepsilon_0\varepsilon r},$$

(1)

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

FIG. 2. (Color online) Room temperature dependence of $(αℏν)^2$ on photon energy $ℏν$ (a), evolution of the PL spectrum with increasing excitation power $P$ (b), and excitation power dependence of the EX peak at 5 K (c).

FIG. 3. (Color online) Temperature dependence of the PL spectra (a), temperature quenching of the integrated intensity of the DAP peak (○, experimental points; -, fitted lines) (b), and dependence of the DAP peak spectral position on temperature (c).
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, $\varepsilon$ is the static dielectric constant, and $\varepsilon_0$ is the permittivity of vacuum. The last term of Eq. (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$_2$. Therefore, DAP$_{1LO}$ and DAP$_{2LO}$ can be assigned to phonon-assisted DAP recombination with a LO phonon energy of $E_{LO} = 28 \pm 2$ meV (226 ± 16 cm$^{-1}$). The experimental uncertainty of determining the spectral position of the DAP bands in the PL spectra is such that the Raman line associated with LO phonons could be merged with the broad feature at 234 cm$^{-1}$.

The PL spectra, shown in Fig. 2(b), also reveal a high-energy feature (labelled 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 with varying excitation power. The spectral position and the excitation power dependent behaviour of the EX feature suggest that this band can be attributed to a recombination of excitons. 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 consists of non-resolved free and bound excitons.

Since the excitonic feature has been observed at liquid helium temperature, whereas the band gap measurements were carried out at room temperature, we cannot 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 XRD and Raman spectra demonstrating high structural quality of CZTSe solar cells. 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, determined 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 it is associated with the optical transitions between an acceptor at 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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