Temperature dependent band-gap energy for $\text{Cu}_2\text{ZnSnSe}_4$: A spectroscopic ellipsometric study

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Abstract

Spectroscopic ellipsometry (SE) is used to study the dependence of the band-gap energy for $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) on temperature ranging from 50 to 350 K. A CZTSe thin film prepared by the *pseudo-bulk* approach allows direct observation of the fundamental band-gap $E_0(\text{A,B})$ in the SE data without need for multi-layer modeling. We obtain accurate energy values for $E_0(\text{A,B})$ and its spin-orbit splitting component $E_0(\text{C})$ from standard lineshape analysis of the second-energy-derivative spectra. The $E_0(\text{A,B})$ and $E_0(\text{C})$ energies for CZTSe decrease with increasing temperature, as for many semiconductors, but **their temperature dependencies are relatively weak. Our experimental observation can be explained in terms of relatively small change in bond-length and strong *p-d* states coupling at the valence band maximum.**

Keywords

$\text{Cu}_2\text{ZnSnSe}_4$; solar cell; Spectroscopic ellipsometry; Band-gap energy

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1. Introduction

An earth-abundant I_{II}-II-IV-VI_I quaternary compound, Cu₂ZnSnSe₄ (CZTSe) is considered a promising absorber material for next-generation thin-film photovoltaic (PV) devices [1-3]. The power conversion efficiency η for CZTSe-based cells has been recorded as high as 9.83 % (open-circuit voltage [V_{oc}] = 0.3798 V, short-circuit current [I_{sc}] = 15.792 mA, and fill factor [FF] = 68.86 %)[4] despite the relatively brief history of CZTSe in thin-film PV technologies.

The fundamental optical properties of constituent materials are of importance for designing a high-performance PV device structure and modeling its performance [3,5]. In particular, the fundamental band-gap energy (E_g) of the absorber layer influences the V_{oc} and thus the η of the resulting device. The experimentally determined E_g value can also be used to verify the predictions made by electronic structure calculations, which in turn can play an important role in further improving device performance through *bandgap engineering* and *defect engineering*.

Most of the electronic-structure calculations are carried out at 0 K. Therefore, taking experimental data at low temperature has a certain benefit for more accurate comparison between the experiments and calculations. The thermal broadening of the optical transition is reduced at low temperature, which helps observe small optical structures more clearly. Furthermore, optical data collected over a wide temperature range offer some additional information, such as (1) estimation of fundamental optical parameters including E_g at arbitrary temperature from interpolation/extrapolation schemes, which can be used to model the device performance at high temperature, and (2) detailed knowledge of electronic transitions and electron-phonon interactions, which helps understand the physical nature of the materials and accurately assign the critical point (CP) structures.

The photoluminescence (PL) technique has been adopted to investigate the temperature-dependent E_g of CZTSe [6,7], but the potential fluctuation caused by various types of defect structures presented in polycrystalline CZTSe thin films makes it complicated to unambiguously identify the physical origin of the main optical structure in the PL spectra and

to understand its temperature dependence [8]. Spectroscopic ellipsometry (SE) accurately determines the optical function spectra of materials over a wide spectral range [9] and is relatively immune to the presence of small amounts of impurities and defects. Therefore, the intrinsic bulk optical properties of CZTSe can be better represented by SE than by PL.

Our previous room-temperature SE study [10] of CZTSe combined with X-ray photoemission spectroscopy focused on the surface chemistry and above-band-gap CP structures. In this article, we report the *pseudodielectric function* $\langle \epsilon \rangle = \langle \epsilon_1 \rangle + i\langle \epsilon_2 \rangle$ spectra of CZTSe determined by SE in the temperature range of 50 to 350 K, with the primary goal of studying the temperature dependence of E_g for CZTSe. Our $\langle \epsilon \rangle$ data clearly show the fundamental band-gap $E_g(A,B)$ structure as well as numerous above-band-gap CP structures. From standard lineshape analysis of SE data [9-12], we establish the energies of $E_g(A,B)$ and its spin-orbit splitting component $E_g(C)$ that are currently lacking in the literature. **The observed relatively weak dependencies of the $E_g(A,B)$ and $E_g(C)$ energies on temperature are discussed.**

2. Materials and methods

2.1. Film growth

A polycrystalline CZTSe thin film was grown by thermal co-evaporation of elemental Cu, Zn, Sn, and Se. Details of the growth can be found in Ref. [13]. The substrate temperature was 506 °C, and the nominal film thickness was 2 μm . The Zn/Sn and Cu/(Zn+Sn) ratios measured by X-ray fluorescence were 1.02 and 0.90 (slightly Cu-poor), respectively.

The film was grown on a soda-lime glass substrate. We mechanically roughened the front surface of the substrate using abrasive alumina powder with a particle size of 9 μm before loading it into the deposition chamber. **The root-mean-square (RMS) roughness of resulting surface determined by atomic force microscopy (AFM) was about 530 nm. A series of alumina powders with different sizes have also been tested, which give different levels of surface roughness. When the resulting surface roughness is too small, the reflected light from the film/ substrate interface still influences the SE data. For example, the alumina powders with a**

particle size of 3 μm result in ~ 140 nm of RMS roughness and the thickness fringes were clearly seen below the absorption edge of CuInGaSe, thin films (not shown). When the surface roughness is too large, on the other hand, the film needs to be grown very thick. In this study, the optimum alumina powder particle size was found to be ~ 9 μm . After the film growth, the CZTSe surface was chemo-mechanically polished using a colloidal suspension of 0.02- μm silica particles to reduce the RMS surface roughness from about 71 to 3 nm [10].

2.2. Spectroscopic ellipsometric measurements

SE data were recorded from 0.74 to 6.43 eV in the temperature range of 50 to 350 K using a dual-rotating compensator-type ellipsometer (J.A. Woollam Inc., RC-2 model) equipped with a variable-temperature cryostat. The angle of incidence was 68° . The sample temperature was carefully monitored using a Si diode temperature sensor physically attached to a small piece of dummy sample, which was mounted next to the actual CZTSe sample on a Cu sample plate.

3. Results and discussion

In SE measurements of thin films grown on a flat surface, the lights reflected from the interface between the film and substrate also reach the detector, as do those reflected from the front surface. The lights reflected from the two different surfaces interfere with each other and generate oscillatory patterns below the E_g of the film. Depending on the absorption coefficient α and the thickness of the film, these patterns may appear even in the spectral range above the E_g . If the optical properties of both the substrate and film are accurately known *a priori*, then the oscillatory patterns can be removed, in principle, by the multilayer modeling procedure, and the film thickness can also be estimated. In practice, however, several non-idealities may exist, such as (1) unidentified thin interfacial layers between the film and substrate, and (2) optical complexities in the substrate including inhomogeneity and anisotropic nature. As a result, the extracted E_g value may be affected by the chosen model parameters, and accurate determination of the film's E_g often becomes a nontrivial task.

To minimize the experimental artifacts in SE data of semiconductor thin films, we developed the *pseudo-bulk* approach, where we first mechanically roughen the front surface of the substrate and then grow a film on it. The probing light penetrating through the film scatters in random directions at the roughened surface of the substrate, which suppresses the *unwanted* secondary reflections from the film/substrate interface, as depicted in Fig. 1(a). Consequently, the CZTSe thin film can now be regarded as a *pseudo-bulk* whose optical thickness is semi-infinite. Figure 1(b) is a cross-sectional scanning electron microscopic image of the CZTSe film used in this study, which also reveals the formation of large grains extending continuously from the film/substrate interface to the surface. We note that the micrograph shown in Fig. 1(b) was taken after chemo-mechanically polishing the CZTSe surface.

Figures 2(a) and 2(b) present the real and imaginary parts of the $\langle \epsilon \rangle$ spectra of CZTSe, respectively, taken at 50, 150, 250, and 350 K. The data taken at 350 K are generally similar to the room-temperature data reported in our previous study [10]. As the temperature decreases, the optical structures are better resolved, particularly in the spectral range of 3.5 to 6.0 eV. A total of six above-band-gap CP structures have been analyzed from 1.5 to 6.5 eV for our previous room-temperature data [10]. A couple of additional CP structures were found in the same spectral region by a preliminary analysis of our new data taken at 50 K. It is complicated to obtain the energy and temperature dependence of those above-band-gap CP structures with a positive identification of their electronic origin, primarily because of the close proximity of several CP structures within a narrow spectral range. A temperature-dependence study of the above-band-gap CP structures will be the subject of a future publication.

Employment of the pseudo-bulk approach and post-growth surface polishing procedure makes the E_g of CZTSe at around 1 eV clearly visible in the $\langle \epsilon_i \rangle$ spectra without need for multilayer modeling. The E_g energy is often estimated by extrapolating the linear segment of the $(\alpha E)^2$ curve as a function of E to zero. However, the linear section of $(\alpha E)^2$ is not always defined unambiguously, and therefore the E_g energy may be determined with a large uncertainty.

To obtain the E_0 energy more accurately, we numerically calculated the second-energy-derivative $d^2\langle\epsilon\rangle/dE^2$ spectra using the linear filtering algorithm of the Savitzky-Golay type [14]. The threshold energies are extracted by fitting the spectra to the standard analytic CP expressions by a least-squares scheme. The expressions are [10-12]:

$$\frac{d^2\epsilon}{dE^2} = \begin{cases} n(n-1)Ae^{i\phi}(E-E_g+i\Gamma)^{n-2}, & n \neq 0 \\ Ae^{i\phi}(E-E_g+i\Gamma)^{-2}, & n = 0 \end{cases} \quad (1)$$

where A is the amplitude, E is the threshold energy, Γ is the broadening parameter, and ϕ is the excitonic phase angle. The exponent n has the values -0.5, 0, and 0.5 for one-, two-, and three-dimensional lineshapes, respectively. Both real (ϵ_r) and imaginary (ϵ_i) parts were fit simultaneously.

Figure 3(a) shows the $d^2\langle\epsilon\rangle/dE^2$ spectra together with the best-fit curves for the 50 K data near the E_0 region (< 1.5 eV). The solid circles and squares represent the real and imaginary parts, respectively, numerically calculated from the experimental data, whereas the solid lines correspond to the best-fit curves. Residual structures are greatly enhanced in the $d^2\langle\epsilon\rangle/dE^2$ spectra, and the $E_0(A,B)$ and $E_0(C)$ CPs are clearly seen in the spectral range of 0.8 to 1.5 eV. The two- and three-dimensional lineshapes are used to fit the $E_0(A,B)$ and $E_0(C)$ CPs, respectively, which results in the lowest mean-square deviation. A small discrepancy between the data and fit curve below 0.9 eV is probably due to the noise presented in experimental data as the energy of probing light approaches to the spectral limit of our system.

Our fit-determined $E_0(A,B)$ CP energy is 0.97 eV at room temperature, which is in a good agreement with the reported E_g values. The E_g of ~ 1 eV was obtained by optical absorption calculated from transmission and reflection data [6] and external quantum efficiency (EQE) measurements [2]. Earlier experimental studies somewhat overestimated the E_g (> 1.4 eV) [15-17], but recent theoretical predictions ($E_g \sim 1$ eV) [18-20] are supportive to our result.

The $E_v(A)$ and $E_v(B)$ CPs are separated mainly by crystal-field (Δ_{cr}) splitting, and the $E_v(A,B)$ and $E_v(C)$ CPs by spin-orbit (Δ_{so}) splitting [18]. The Δ_{cr} value has been predicted to be about 7 meV for kesterite-phase CZTSe [18], which is below the spectral resolution of our data. This is consistent with our observation that the $E_v(A)$ and $E_v(B)$ CPs appear as a singlet in our data. However, the calculated Δ_{so} value [18] of about 0.2 eV is large enough to be observed experimentally in this study. Our SE data suggest that the Δ_{so} value for CZTSe at 50 K is about 0.3 eV, which is slightly larger than the theoretical prediction. The small discrepancy could be caused by overestimation of p - d coupling in the theoretical calculation or caused by off crystalline stoichiometry of the experimental sample.

The temperature dependencies of the $E_v(A,B)$ and $E_v(C)$ energies are analyzed by fitting the data to the single Bose-Einstein oscillator [21]:

$$E(T) = E(0) - a \left[1 + \frac{2}{\exp[\frac{\Theta}{T}] - 1} \right] \quad (2)$$

where $E(0)$ is the energy at 0 K, and a is a parameter associated with the strength of electron-phonon interactions within the crystal, which describes the degree of the E decrease with increasing temperature. Θ is the average temperature of phonons interacting with the electronic system, which is essentially the average energy of phonons divided by the Boltzmann constant (k_B). The data and best-fit curves are shown as solid circles and solid lines, respectively, in Fig. 3(b), and the fit-determined parameters $E(0)$, a , and Θ are listed in Table I.

As for many semiconductors [22], the E_v energy of CZTSe decreases with increasing temperature, but the change seems to be relatively small for CZTSe, as shown in Fig. 3(b). For semiconductors, dependence of the E_v energy on temperature is influenced largely by two factors: (1) the change in bond length via the volume deformation and (2) the change in electron-phonon interactions [23]. It has been shown [24] that the change in E_v energy with

volume deformation is relatively small for Cu-containing chalcopyrite semiconductors, such as $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGSe), compared to zinc-blende ones. For chalcopyrite semiconductors, which possess relatively large structural freedom, the interatomic distances (i.e., bond lengths) are less affected by changes of unit-cell volume because the bond lengths can be adjusted by changing the internal coordinates of the cell u [24]. In addition, for Cu-containing compounds with a large anion p and Cu d coupling, the volume effect is largely cancelled by the p - d coupling effect, as the effects have opposite signs [24]. A weak dependence of CP energies on temperature for CIGSe has indeed been observed by SE [25]. Considering the similarities in the structural and electronic properties between chalcopyrite-phase CIGSe and kesterite-phase CZTSe, it is not surprising to observe that a similar weak temperature dependence of the $E_v(\text{A,B})$ and $E_v(\text{C})$ CP energies also exists for CZTSe.

The relatively weak electron-phonon interaction, as reflected by the small a value in Table I, can be partly attributed to the strong ionic characteristic of CZTSe. The s - s coupling that determines the conduction-band-minimum volume deformation and the p - p coupling that determines the valence-band-maximum volume deformation are both small in magnitude for CZTSe. In addition, a large anion- p and Cu- d coupling also reduces the valence-band-maximum volume deformation because the effect of p - d coupling is against the normal p - p coupling. The a parameter for $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has been reported to be 55.9 meV [26] and 90.25 meV [27] obtained by transmittance measurements, which are a few times larger than that for CZTSe determined in our study. The observed difference in the a parameter between CZTS and CZTSe is expected. S-containing compounds have higher phonon frequency, thus larger Θ value than the corresponding Se-containing ones, while the $dE(T)/dT$ values for the two compounds are very close [28]. Similar difference has been observed between CuGaSe_2 ($a = 23$ meV) [29] and CuGaS_2 ($a = 54 - 88$ meV) [30].

It is interesting to note in Fig. 3(b) that the temperature dependence of E_v for CZTSe shows an extended plateau in the low-temperature region (< 100 K) but changes faster at higher temperature. This can be understood by considering that the number of phonons is limited at

low temperature, so the temperature dependence of E_0 is dominated by the volume and p - d coupling effects, which nearly cancel each other, as discussed above. However, as the temperature increases, more phonons are excited, and thus the electron-phonon interaction is enhanced. Consequently, the E_0 decreases faster as the temperature increases in the high-temperature region. It is noteworthy that Luckert *et al.* [6] reported a non-monotonic temperature dependence of the PL peak energy for CZTSe. Even though the magnitude of change is small, they observed that the PL energy initially increases up to 30 K with increasing temperature and then decreases in the higher-temperature region. Owing to the presence of various types of defect structures, however, the physical origin of the PL peak and temperature-dependent PL peak energy have not been fully discussed.

4. Conclusions

The energies of the fundamental band-gap $E_0(A,B)$ and its spin-orbit splitting component $E_0(C)$ for $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and their temperature dependencies were determined by spectroscopic ellipsometry in the temperature range of 50 to 350 K. As the temperature increases, the $E_0(A,B)$ and $E_0(C)$ energies do not ostensibly change up to 100 K, above which they decrease slowly. The observed **weak** temperature dependence of E_0 for CZTSe can be explained by the large structural freedom in the kesterite structure, the p - d electron level repulsion, and the temperature dependence of the electron-phonon coupling. The results from our study on CZTSe help better understand the electronic structures and related optical properties of kesterite-phase thin-film photovoltaic materials, and can also be compared to results from previous studies on similar classes of materials, such as Cu-containing chalcopyrite semiconductors.

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TABLE I. Parameters for the Bose-Einstein oscillator $E(0)$, a , and Θ obtained by fitting the $E_0(A,B)$ and $E_0(C)$ energies to Eq. (2).

CP	$E(0)$ [eV]	a [eV]	Θ [K]	Lineshape
$E_0(A,B)$	1.013 ± 0.005	0.023 ± 0.005	397.8 ± 54.7	2-D ($n = 0$)
$E_0(C)$	1.310 ± 0.006	0.021 ± 0.006	365.6 ± 70.3	3-D ($n = 0.5$)

Figure Captions

FIG. 1. (Color online) (a) Schematic and (b) cross-sectional scanning electron micrograph of CZTSe thin film grown on roughened glass surface. The probing light reaches the interface between the film and substrate and is scattered in random directions. The resulting CZTSe thin film can be regarded as a *pseudo-bulk* material.

FIG. 2. (Color online) (a) Real and (b) imaginary parts of the ϵ spectra for CZTSe, respectively, taken at 50, 150, 250, and 350 K. For clarity, the spectra are offset upward from the 350 K spectra by an increment of 0.6.

FIG. 3. (Color online) (a) Red and blue solid lines: standard CP lineshapes best fit to second-energy-derivatives $d^2\langle\epsilon_i\rangle/dE^2$ (solid circles) and $d^2\langle\epsilon_i\rangle/dE^2$ (solid squares), respectively, for the data taken at 50 K. Energies of $E_o(A,B)$ and $E_o(C)$ are indicated by arrows. (b) Dependencies of $E_o(A,B)$ and $E_o(C)$ energies on temperature from 50 K to 350 K. Solid circles are the fit-determined energies as shown in (a), and solid lines represent the best fits of energies to the Bose-Einstein oscillator (Eq. (2)).

Figure 1

Figure 2

Figure 3