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Dielectric function spectra and critical-point energies of $\text{Cu}_2\text{ZnSnSe}_4$ from 0.5 to 9.0 eV

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We present dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ spectra and critical-point energies of $\text{Cu}_2\text{ZnSnSe}_4$ determined by spectroscopic ellipsometry from 0.5 to 9.0 eV. We reduce artifacts from surface overlayers to the maximum extent possible by performing chemical-mechanical polishing and wet-chemical etching of the surface of a $\text{Cu}_2\text{ZnSnSe}_4$ thin film. Ellipsometric data are analyzed by the multilayer model and the ε spectra are extracted. The data exhibit numerous spectral features associated with critical points, whose energies are obtained by fitting standard lineshapes to second energy derivatives of the data. The experimental results are in good agreement with the ε spectra calculated within the *GW* quasi-particle approximation, and possible origins of the pronounced critical-point structures are identified. © 2012 American Institute of Physics. [doi:10.1063/1.3681814]

I. INTRODUCTION

There is an increasing interest^{1–4} in the quaternary compounds $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) for their applications in thin-film photovoltaic (PV) devices. The material's bandgap energy in the range of 1.0–1.5 eV and high absorption coefficient of $\sim 10^4 \text{ cm}^{-1}$ are suitable for high-performance PV devices, and the earth-abundance of the constituent elements paves a new pathway for gigawatt-scale mass production of PV.¹ In addition, the non-toxic nature of the elements also eliminates environmental concerns.

Despite their brief history in thin-film PV, CZT(S,Se) technologies are rapidly advancing and their conversion efficiency has already reached as high as 10.1%.² Knowledge of the optical properties of materials, such as dielectric functions $\varepsilon = \varepsilon_1 + i\varepsilon_2$ and refractive index $N = n + ik = [\varepsilon]^{1/2}$, is important to develop and optimize PV device structure, as well as to improve our understanding of the electronic structure and related physical characteristic.⁵ For example, the N (or ε) is one of the input parameters for optical modeling of PV device performance, and the ε spectra are widely used to verify the predictions made by the electronic structure calculations.⁶ Surprisingly, however, the properties of CZTSe have not yet been explored in great detail. In particular, experimental studies are relatively rare and previous studies have focused mainly on determining the bandgap energy³ and probing the secondary phases.⁴

Here, we apply spectroscopic ellipsometry (SE) to investigate the optical properties of CZTSe. SE is recognized⁷ as a highly suitable method of determining the ε and N spectra of materials over a wide spectral range. The sur-

face sensitivity of this technique, however, often makes it complicated to obtain a material's intrinsic properties when surface overlayers are present.⁸ Because optical information on overlayers is usually unavailable *a priori*, mathematical modeling of SE data without sufficient knowledge can potentially lead to inaccurate results. In this study, we attempt to reduce overlayer artifacts by performing chemical-mechanical polishing (CMP) and wet-chemical etching of the surface before SE measurements.

The ε data exhibit numerous optical structures associated with critical points (CPs) and their energies are obtained by the standard line shape analysis.⁹ The experimental data are in good agreement with the spectra calculated in the *GW*-random phase approximation (RPA).¹⁰ We identify the possible origins of the prominent CP structures observed in the ε spectra in this work.

II. EXPERIMENTS

A polycrystalline CZTSe thin film was grown by thermal co-evaporation of elemental Cu, Zn, Sn, and Se. The substrate was soda-lime glass coated with a 1- μm -thick molybdenum (Mo) film, and its temperature was held at 490 °C during growth. The nominal thickness of the film was 1.5 μm . X-ray fluorescence was used to determine chemical composition, which was calibrated by inductively coupled plasma optical emission spectrometry. The film turned out to be slightly Zn-rich ($\text{Zn}/\text{Sn} = 1.07$) and Cu-poor ($\text{Cu}/[\text{Zn} + \text{Sn}] = 0.96$). The film's structural properties were characterized by X-ray diffraction, Raman scattering spectroscopy, and Auger electron spectroscopy, which showed no clear evidence of the secondary phases, such as ZnSe and Cu_2SnSe_3 , within the film. Detailed discussions on the growth and phase identification are given elsewhere.^{11,12}

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The surface roughness was greatly reduced by CMP procedures using a colloidal silica suspension with 0.02- μm particles. We attempted to further remove the residual oxides as much as possible by etching the film surface with a 50 vol % solution of NH_4OH in DI water (AmH) for 30 s in air. Changes of the morphology and chemistry of the CZTSe surface were monitored by atomic force microscopy (AFM) and X-ray photoemission spectroscopy (XPS), respectively. AFM images were recorded in air by using a Digital Instrument – Dimension 3100 model equipped with Nanoscope-V controller. XPS spectra were taken in a Physical Electronics 5600 photoemission system using monochromatic $\text{Al K}\alpha$ radiation, a 45° take-off angle, and an 800 μm slit. The pass energy was 29.35 eV, and the dwell time per data point was 2 s.

A variable-angle rotating compensator SE (J.A. Woollam Inc., M-2000 DI model) was used to assess the surface conditions in the spectral range from 0.74 to 6.45 eV. The incident angle was varied from 55° to 75° with an increment of 5° . We minimized recontamination of the surface by continuously flowing N_2 gas onto the sample during the measurements. The full $\langle \varepsilon \rangle$ spectra were then separately acquired from 0.5 to 9.0 eV with the sample at room temperature by using a vacuum-ultraviolet (VUV) SE, which is a rotating analyzer type equipped with a computer-controlled MgF₂ Berek compensator. The angle of incidence was 70° .

III. COMPUTATIONAL DETAILS

Theoretical analysis of the total dielectric function $\varepsilon = [2\varepsilon_\perp + \varepsilon_\parallel]/3$ spectra is performed using the ε data reported in Ref. 10, which were calculated within the *GW* approximation.¹³ This first-principles method is developed to calculate the energies and self-energies of electrons in a solid by updating both Green's functions *G* and screened Coulomb potential *W* in the self-consistent approach. The *GW* approximation can be regarded as a generalization of the Hartree-Fock approximation but with a dynamically screened Coulomb interaction. In this work, we analyze the ε spectra and identify the CPs of the photon-assisted transitions.

CZTSe crystallizes in either the kesterite (KE) structure with the space group of $I\bar{4}$ or the stannite (ST) with the space group of $I\bar{4}2m$, which can be distinguished by the relative positions of Cu and Zn atoms in the unit cell.¹⁴ The ordering of cations was taken into account, and ε spectra of CZTSe were calculated for both structures.¹⁰

CP structures observed in the ε spectra are associated with Van Hove singularities (VHSs) in the joint density of states (JDOS), defined as⁹

$$D_j(E) = \frac{1}{4\pi^3} \int_{\text{BZ}} \frac{dS_{\mathbf{k}}}{|\nabla_{\mathbf{k}}[E_{\text{cv}}(\mathbf{k})]|}, \quad (1)$$

where $S_{\mathbf{k}}$ is the constant energy surface of optical transition energy $E_{\text{cv}}(\mathbf{k}) = E_{\text{c}}(\mathbf{k}) - E_{\text{v}}(\mathbf{k})$. The CPs in ε spectra are mapped to critical $\mathbf{k}$ -points in the JDOS where the gradients of E_{cv} vanish. In our calculations, four possible high-symmetry $\mathbf{k}$ -points (HSKPs), $\Gamma(0, 0, 0)$, $Z(0, 0, 1/2)$, $X(1/2, 1/2, 0)$, and $P(1/2, 1/2, 1/2)$ are considered.

Assuming parabolic curvature of the valence and conduction bands, E_{cv} can be expanded in the vicinity of the HSKP $\mathbf{k}_0$ to the second order of $\mathbf{u} = \mathbf{k} - \mathbf{k}_0$ as

$$E_{\text{cv}}(\mathbf{k}) = E_{\text{cv}}(\mathbf{k}_0) + \gamma_\perp u_\perp^2 + \gamma_\parallel u_\parallel^2 + O(u^4), \quad (2)$$

with

$$\gamma_i = \frac{1}{2} \frac{\partial^2 E_{\text{cv}}}{\partial k_i^2} = \frac{\hbar^2}{2} \left(\frac{1}{m_i^{e*}} + \frac{1}{m_i^{h*}} \right), i = \perp, \parallel, \quad (3)$$

where m^{e*} and m^{h*} are the effective masses of electrons and holes, respectively. The peaks in the ε_2 spectrum correspond to negative values of $d^2 \langle \varepsilon_2 \rangle / dE^2$, implying saddle points of $E_{\text{cv}}(\mathbf{k}_0)$ and thus $\gamma_\perp, \gamma_\parallel < 0$.⁹ To understand the nature of the individual CPs, the effective masses need to be analyzed at the HSKPs. For the calculations of the effective masses, we used a dense *k*-mesh and the generalized gradient approximation (GGA) with the onsite Coulomb correction $U_d(\text{Cu}) = 4$ eV, $U_d(\text{Zn}) = 6$ eV, and $U_s(\text{Se}) = -3$ eV. The resulting Γ -point electron masses ($m_\perp^{e*} = 0.08m_0$ and $m_\parallel^{e*} = 0.09m_0$) agree well with the previously reported values.¹⁵

IV. RESULTS AND DISCUSSION

AFM images of the CZTSe surface before and after the CMP procedures are compared in Figs. 1(a)–1(d). The length scale of the *x*- and *y*-axis for all the images shown here is 5 μm . The plan-view images are rendered in an 8-bit gray scale with black on this scale corresponding to the reference height (0 nm) in the *z*-axis. The maximum *z*-height values for Figs. 1(a) and 1(c), which are mapped to the color white,

FIG. 1. AFM images of the “as grown” surface ((a) and (b)) and the chemical-mechanical polished surface followed by the AmH rinse ((c) and (d)). (a) and (c) are plan-view images while (b) and (d) are 3-D views constructed from the corresponding plan-view images. The estimated surface roughness values for “as grown” and “polish + AmH” surfaces are 70.9 and 2.7, respectively. Note: Side-length of all the images shown here is 5 μm . The plan-view images are rendered in an 8-bit gray scale, and black on this scale corresponds to the reference height (0 nm) in the *z*-axis. The maximum *z*-height values for Figs. 1(a) and 1(c), which are mapped to the color white, are 398 and 17.1 nm, respectively.

are 398 and 17.1 nm, respectively. The CMP procedures greatly reduced the root-mean-square (RMS) roughness from 70.9 nm for the “as grown” surface (Figs. 1(a) and 1(b)) down to 2.7 nm for the “Polish and AmH” surface (Figs. 1(c) and 1(d)).

Figure 2 is comprised of XPS data for the polished and polished/AmH surfaces. A general spectral feature of the AmH-washed surface is a reduction of the full-width-at-half-maximum (FWHM) values for the various core levels, indicating a reduction in the number of chemical states. As seen in O 1s spectra, the relative amount of surface oxygen decreased by about 50% after AmH treatment. The Se 3d region shows that the high binding energy peaks (Se 3d_{5/2} = 58.7 eV) corresponding to Se⁴⁺ species such as selenates have been removed. High binding energy shoulders observed in the Cu 2p_{3/2} and Sn 3d_{5/2} spectra of the polished surface were also removed by the AmH treatment, which are indicated by arrows in Figs. 2(c) and 2(d). Our XPS data thus suggest that AmH washing removes some of the native oxides found on

FIG. 2. (Color online) XPS spectra of (a) O 1s, (b) Se 3d, (c) Cu 2p_{3/2}, (d) Sn 3d_{5/2}, and (e) Zn 2p_{3/2} peaks for the polished CZTSe surface taken before (dotted red lines) and after (solid black lines) the AmH treatment. Suppression of the O 1s peak and disappearance of the Se⁴⁺ peak indicate the positive effects of AmH treatments on the removal of native oxides from the CZTSe surface. The peaks on the high binding energy side of the main lines for the Sn, Cu, Zn, and Se core levels have also been removed by the AmH treatment, which are indicated by arrows for Cu 2p_{3/2} and Sn 3d_{5/2} core levels in (c) and (d).

the CZTSe surface, as has been found for other selenide surfaces.^{16,17}

The SE-determined imaginary part of the pseudodielectric function $\langle \varepsilon \rangle = \langle \varepsilon_1 \rangle + i \langle \varepsilon_2 \rangle$ spectra is given in Fig. 3, which also clearly reflects the positive roles of the CMP procedure and AmH treatment in the improvement of the CZTSe surface. The $\langle \varepsilon_2 \rangle$ spectrum, especially in the high energy region, is sensitive to the presence of surface overlayer, and the $\langle \varepsilon_2 \rangle$ value is reduced from its intrinsic ε_2 value. The magnitude of difference $\varepsilon_2 - \langle \varepsilon_2 \rangle$ is roughly proportional to the thickness of the overlayer.⁸ The CP structure at ~ 2.5 eV appeared distinctly in the “polished” spectrum is not obvious in the “as-grown” spectrum, which is perhaps obscured by the thick surface overlayers. In addition, significant enhancement of the CP structures at ~ 4 and ~ 5 eV in the $\langle \varepsilon_2 \rangle$ spectra, which is further improved by AmH treatment, indicates the successful reduction of surface overlayers in accordance with previous SE studies.^{8,16,18} Large oscillations below ~ 1.3 eV are the thickness fringes from the transparent characteristic of the film below its fundamental absorption edge.^{18,19}

A VUV-SE measurement was carried out over an extended photon energy range from 0.5 to 9.0 eV to acquire the $\langle \varepsilon \rangle$ spectra of CZTSe after the CMP procedures and AmH treatment of the surface. To obtain the ε of CZTSe with the mathematical corrections for the presence of residual surface overlayers and thickness fringes, the $\langle \varepsilon \rangle$ data were analyzed by a multilayer model consisting of the ambient, a surface-roughness layer, the CZTSe layer, and the Mo buffer layer. The soda-lime glass substrate was not included in the model because its presence was completely obscured by the 1- μ m-thick metallic Mo layer in the spectral range of our measurements. The surface-roughness layer, represented by a Bruggeman effective medium approximation,²⁰ was estimated to be ~ 3.0 nm.

FIG. 3. (Color online) Effects of surface polishing and chemical treatments on $\langle \varepsilon_2 \rangle$ of CZTSe. Polishing (dotted black line) and AmH (solid red line) treatment improve the data and the optical structures are better resolved. Data for the “as-grown” surface are represented by the dashed green curve.

FIG. 4. (Color online) (a) Real and (b) imaginary parts of SE-determined ϵ spectra (solid black lines) compared to the spectra for kesterite (dashed red lines) and stannite (dotted blue lines) structures calculated within the GW approximation. Five CP structures are observed in the SE data that are indicated by upward arrows. The corresponding CP structures, identified in the calculated data, are indicated by downward arrows. Note: Two weak CP structures E_2 and E_3 are resolved in the derivative spectra (see Fig. 5).

The ϵ of CZTSe layer was constructed by the B-spline formulation.²¹ A spline function is basically a series of polynomial segments, which is constructed in a manner to maintain continuity up to a certain degree of differentiation. B-splines are a basis set for polynomial splines, and this set of basis functions can describe optical structure in the ϵ_2 spectrum while providing the Kramers-Kronig consistent dispersion ϵ_1 spectrum at the same time.

The real and imaginary parts of the resulting ϵ spectra are shown as solid black lines in Figs. 4(a) and 4(b), respectively. For comparison, the calculated ϵ spectra of CZTSe in the KE and ST structures are also shown as dashed red lines and dotted blue lines, respectively.¹⁰ Both the KE and the ST structures belong to the body-centered tetragonal Bravais lattice. Therefore, they exhibit similar CP structures in the ϵ spectra with small differences in the CP energies. The agreement between the data and calculations is overall very reasonable, and the major CP structures at around 2.5, 4.0, 5.0, 6.0, and 7.0 eV in the SE data are all identified in the calculations, as indicated by the arrows.

However, a few interesting discrepancies are found as well. SE-determined $\epsilon_\infty = 9.2$ is between the two calculated values¹⁰ for KE (10.31) and ST (8.88) structures. In addition, the amplitudes of the E_1 peak in the ϵ_2 spectra are similar for the SE results and the calculated value of the ST structure, whereas that of KE is about twice as large. Those observations suggest that the CZTSe film used in this study possibly contains both KE and ST structures. In fact, a first-principles

FIG. 5. (Color online) Best-fit curves of the second derivatives of $\langle \epsilon_1 \rangle$ (solid red line) and $\langle \epsilon_2 \rangle$ (dashed-dotted blue line) of CZTSe. The red circles are the numerically calculated $d^2 \langle \epsilon_1 \rangle / dE^2$ data. To clearly show the quality of the fits, $d^2 \langle \epsilon_2 \rangle / dE^2$ data are not shown.

calculation²² has shown that a small difference in formation energy (3 meV/atom) allows the KE and ST structures to coexist even at low temperature. On the other hand, we also note that some previous experimental studies^{23,24} probed the pure KE structure in a similar material, CZTS film. Because of the similarities in the lattice structure as well as the chemistry of the two structures, it is unfortunately very difficult to unambiguously discern the lattice type of a polycrystalline CZTSe. For a positive identification of the lattice structure of our CZTSe thin film, a more systematic structural analysis is required, which is beyond the scope of this work.

To obtain energies of the CP structures observed in Fig. 4, we numerically calculated the second-energy-derivative $d^2 \langle \epsilon \rangle / dE^2$ spectra using linear filtering algorithms of the Savitzky-Golay-type.²⁵ The CP energies are extracted by fitting the spectra to the standard analytic CP expressions by least-squares scheme. These standard expressions are⁹

$$\frac{d^2 \epsilon}{dE^2} = \begin{cases} n(n-1)Ae^{i\phi}(E-E_g+i\Gamma)^{n-2}, & n \neq 0 \\ Ae^{i\phi}(E-E_g+i\Gamma)^{-2}, & n = 0 \end{cases}, \quad (4)$$

where A is the amplitude, E_g is the threshold energy, Γ is the broadening parameter, and ϕ is the excitonic phase angle. For $A > 0$, the values $n = -1, -1/2, 0, 1/2$ represent

TABLE I. CP energies of CZTSe (in eV) obtained from SE measurements. Calculated CP energies for KE and ST (in parentheses) structures are also given with the identification of possible interband transitions. $v_i \Rightarrow c_j$ represents a transition from the i th valence band to the j th conduction band. Here, the v_1 and c_1 denote the topmost valence and bottommost conduction bands, respectively.

CPs	Expt.	Calc. KE (ST)	Transitions
E_1	2.42 ± 0.02	2.34 (2.57)	Z: $v_{1,2} \Rightarrow c_1$
E_2	3.51 ± 0.04	3.52 (4.00)	Z: $v_{1,2} \Rightarrow c_{2,3,4}$
E_3	4.01 ± 0.09	4.22 (4.94)	Γ : $v_{1,2} \Rightarrow c_5$; Z: $v_{7,9} \Rightarrow c_1$
E_4	4.58 ± 0.06	5.16 (5.68)	Γ : $v_{1,2} \Rightarrow c_6$; Z: $v_{1,2} \Rightarrow c_6$, $v_7 \Rightarrow c_4$; X: $v_2 \Rightarrow c_5$, $v_1 \Rightarrow c_4$
E_5	5.26 ± 0.16	5.96 (6.49)	X: $v_4 \Rightarrow c_5$, $v_{9,10} \Rightarrow c_3$; P: $v_4 \Rightarrow c_5$
E_6	5.93 ± 0.06	6.76 (7.00)	P: $v_{11,12} \Rightarrow c_3$, $v_7 \Rightarrow c_4$
E_7	6.87 ± 0.08	7.05 (7.43)	X: $v_6 \Rightarrow c_6$; P: $v_2 \Rightarrow c_8$, $v_{9,10} \Rightarrow c_4$

excitonic, 1-, 2-, and 3-D lineshapes, respectively. Both the real and imaginary parts were fitted simultaneously.

The calculated $d^2 \langle \epsilon \rangle / dE^2$ spectra together with the best-fit curves are shown in Fig. 5. The open circles represent data for $d^2 \langle \epsilon_1 \rangle / dE^2$. For clarity, $d^2 \langle \epsilon_2 \rangle / dE^2$ results are not shown, but the quality of the fits is similar. The solid and dashed-dotted lines are the best-fit curves for the real and imaginary parts, respectively. Sensitivity to the residual feature is greatly enhanced in the derivative spectra, and the two weak CPs, E_2 and E_5 , are now resolved. The E_1 , E_2 , and E_3 CPs are fit best with the excitonic lineshapes ($n = -1$), while the remaining CPs are represented by the 3-D lineshapes ($n = 1/2$). The CP energies obtained are listed in Table I.

Identification of the physical origins of the optical structures plays an important role in better understanding the material's electronic structure and the relative strength of transitions at room temperature. This is in turn important to develop new compounds with desired functionality and predict the effects of impurities and strain engineering on the properties of host materials.

The possible origins of the CP structures are identified from the calculated spectra¹⁰ using the GGA effective masses. We find that the first two CPs, E_1 and E_2 , occur at the Z-point of BZ. The corresponding band-to-band transitions are suggested in Table I. The ϵ_2 data exhibit a strong local maximum at the E_1 CP because of its low-dimensional characteristic at VHS. By decomposing the density of states to atomic site and angular momentum, we find that the E_1 CP structure consists of $\text{Cu}(3d_{xz} + 3d_{yz}) \rightarrow \text{Se}(4p_z)$, $\text{Se}(4p_x + 4p_y) \rightarrow \text{Cu}(3d_x^2 + 3d_{x-y}^2)$, and $\text{Se}(4p_x + 4p_y) \rightarrow \text{Sn}(5s)$ transitions. The net effect is that the $\text{Cu}(3d)$ electrons are excited to $\text{Sn}(5s)$ orbit. Since the d - s dipole transition is forbidden by the selection rule, the $\text{Se}(4p)$ orbital is utilized as a pipe in this process. The E_2 CP involves the $\text{Cu}(3d_{xy} + 3d_{xz}) \rightarrow \text{Sn}(5p_x)$, $\text{Cu}(3d_{xy} + 3d_{yz}) \rightarrow \text{Sn}(5p_z)$, and $\text{Cu}(3d_{yz} + 3d_{xz}) \rightarrow \text{Sn}(5p_z)$ transitions. The net transition is $\text{Cu}(3d) \rightarrow \text{Sn}(5p)$.

The E_3 CP contains the $\text{Cu}(3d) \rightarrow \text{Sn}(5s)$ transition at the Z-point, which is very similar to the E_1 CP. It can be explained as follows: Analogous to the $\text{Cu}(\text{In,Ga})\text{Se}_2$ compound,²⁶ the $\text{Cu}(3d)$ state in CZTSe spans over a large energy range (~ 6 eV) of the upper valence band and splits into two peaks in the density of states spectrum due to the p - d repulsion. The E_1 and E_3 CPs correspond to the transitions from the upper and lower $\text{Cu}(3d)$ peaks to $\text{Sn}(5s)$ state, respectively. Besides, the E_3 CP also contains other possible contributions, i.e., $\text{Cu}(3d_{xy} + 3d_{xz}) \rightarrow \text{Sn}(5p_x)$ and $\text{Cu}(3d_{xy} + 3d_{yz}) \rightarrow \text{Sn}(5p_y)$ occurring at the Γ -point.

High-energy transitions E_4 , E_5 , E_6 , and E_7 CPs contain numerous contributions with different types of transitions occurring over a wide region of BZ, so the amplitudes of these CP structures become relatively large. Due to the close locations of multiple transitions, however, it is challenging to analyze these CPs in a systematic fashion. Possible transitions associated with each CP structure are listed in Table I.

Finally, we discuss possible reasons for the discrepancies observed in the CP energies between the data and calculations. First, the GW quasi-particle approximation partly

neglects the true many-particle interactions, for example the four-point interactions, in describing the excitation effects. As a consequence, the peaks in the calculated ϵ_2 spectrum tend to appear at higher energies than those in the experimental data. A similar trend has also been observed in the previous studies.^{18,27} In addition, the theoretical analysis is based on a zero-temperature model, while the experiments are carried out at room temperature.

V. CONCLUSIONS

Dielectric function ϵ spectra of polycrystalline $\text{Cu}_2\text{ZnSnSe}_4$ have been determined by spectroscopic ellipsometry from 0.5 to 9.0 eV. We performed chemical-mechanical polishing and wet-chemical etching of the surface to obtain $\langle \epsilon \rangle$ data least influenced by surface overlayers. We then extracted ϵ spectra using multilayer modeling procedures. Our $\langle \epsilon \rangle$ data exhibit seven above-bandgap critical-point structures, and their energies are obtained by the standard line shape analysis. The data show good agreement with the ϵ spectra calculated within the GW approximation, and the possible origins of the critical-point structures are identified. The optical function spectra reported in this work can be used to design the CZTSe-related PV devices and model their performance. The energy of critical point structures and their physical origins, on the other hand, will help our better understanding of the electronic structure of CZTSe and the dominant optical transitions at room temperature.

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¹T. K. Todorov, K. B. Reuter, and D. B. Mitzi, *Adv. Mater.* **22**, E156 (2010).

²D. Barkhouse, O. Gunawan, T. Gokmen, T. Todorov, and D. B. Mitzi, *Prog. Photovoltaics* **20**, 6 (2012).

³S. Ahn, S. Jung, J. Gwak, A. Cho, K. Shin, K. Yoon, D. Park, H. Cheong, and J. H. Yun, *Appl. Phys. Lett.* **97**, 021905 (2010), and references therein.

⁴A. Redinger, K. Hönes, X. Fontané, V. Izquiero-Roca, E. Saucedo, N. Valle, A. Pérez-Rodríguez, and S. Siebentritt, *Appl. Phys. Lett.* **98**, 101907 (2011).

⁵M. Law, M. C. Beard, S. Choi, J. M. Luther, M. C. Hanna, and A. J. Nozik, *Nano Lett.* **8**, 3904 (2008).

⁶See, for example, S. Adachi, *Optical Constants of Crystalline and Amorphous Semiconductors: Numerical Data and Graphical Information* (Kluwer, Boston, 1999).

⁷D. E. Aspnes, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, Orlando, 1985), Vol. I, p. 89.

⁸D. E. Aspnes and A. A. Studna, *Appl. Phys. Lett.* **39**, 316 (1981).

⁹M. Cardona, in *Modulation Spectroscopy, Suppl. 11 of Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969).

¹⁰H. Zhao and C. Persson, *Thin Solid Films* **519**, 7508 (2011).

¹¹I. Repins, N. Vora, C. Beall, S.-H. Wei, Y. Yan, M. Romero, G. Teeter, H. Du, B. To, M. Young, and R. Noufi, *Mater. Res. Soc. Symp. Proc.* **1324**, 97 (2012).

¹²N. Vora, I. Repins, C. Beall, B. To, G. Teeter, J. Blackburn, J. Pankow, and R. Noufi, "Phase identification and control of thin films deposited by co-evaporation of elemental Cu, Zn, Sn, and Se" (submitted).

- ¹³L. Hedin, *Phys. Rev.* **139**, A796 (1965).
- ¹⁴S. R. Hall, J. T. Szymanski, and J. M. Stewart, *Can. Mineral.* **16**, 131 (1978).
- ¹⁵C. Persson, *J. Appl. Phys.* **107**, 053710 (2010).
- ¹⁶Y. D. Kim, S. L. Cooper, M. V. Klein, and B. T. Jonker, *Appl. Phys. Lett.* **62**, 2387 (1993).
- ¹⁷B. Canava, J. F. Guillemoles, J. Vigneron, D. Lincot, and A. Etcheberry, *J. Phys. Chem. Solids* **64**, 1791 (2003).
- ¹⁸S. G. Choi, M. van Schilfgaarde, D. E. Aspnes, A. G. Norman, J. M. Olson, T. J. Peshek, and D. H. Levi, *Phys. Rev. B* **83**, 235210 (2011).
- ¹⁹M. Garriga, M. Cardona, N. E. Christensen, P. Lautenschlager, T. Isu, and K. Ploog, *Phys. Rev. B* **36**, 3254 (1987).
- ²⁰G. E. Jellison Jr., L. A. Boatner, D. H. Lowndes, R. A. McKee, and M. Godbole, *Appl. Opt.* **33**, 6053 (1994).
- ²¹B. Johs and J. S. Hale, *Phys. Status Solidi A* **205**, 715 (2008).
- ²²S. Y. Chen, X. G. Gong, A. Walsh, and S. H. Wei, *Appl. Phys. Lett.* **94**, 041903 (2009).
- ²³S. Schorr, *Sol. Energy Mater. Sol. Cells* **95**, 1482 (2011).
- ²⁴P. K. Sarswat, M. L. Free, and A. Tiwari, *Phys. Status Solidi B* **248**, 2170 (2011).
- ²⁵A. Savitzky and M. J. E. Golay, *Anal. Chem.* **36**, 1627 (1964).
- ²⁶S. B. Zhang, S. H. Wei, A. Zunger, and H. Katayama-Yoshida, *Phys. Rev. B* **57**, 9642 (1998).
- ²⁷M. Rohlifing and S. G. Louie, *Phys. Rev. B* **62**, 4927 (2000).