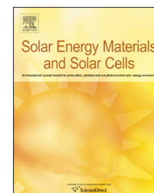
Solar Energy Materials & Solar Cells 130 (2014) 375–379

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Temperature dependent band-gap energy for $Cu_2ZnSnSe_4$: A spectroscopic ellipsometric study

S.G. Choi [a,*], T.J. Kim [b], S.Y. Hwang [b], J. Li [a,c], C. Persson [d], Y.D. Kim [b], S.-H. Wei [a], I.L. Repins [a]

[a] National Renewable Energy Laboratory, Golden, CO 80401, USA
[b] Department of Physics, Kyung Hee University, Seoul 130-701, Republic of Korea
[c] Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606, USA
[d] Department of Physics, University of Oslo, N-0316 Oslo, Norway

ARTICLE INFO

Article history:
Received 12 December 2013
Received in revised form
21 May 2014
Accepted 22 July 2014

Keywords:
$Cu_2ZnSnSe_4$ solar cell
Spectroscopic ellipsometry
Band-gap energy

ABSTRACT

Spectroscopic ellipsometry (SE) is used to study the dependence of the band-gap energy for $Cu_2ZnSnSe_4$ (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(A,B) in the SE data without need for multi-layer modeling. We obtain accurate energy values for E_0(A,B) and its spin–orbit splitting component E_0(C) from standard lineshape analysis of the second-energy-derivative spectra. The E_0(A,B) and E_0(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.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

An earth-abundant I_2–II–IV–VI_4 quaternary compound, $Cu_2ZnSnSe_4$ (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_0) of the absorber layer influences the V_{oc} and thus the η of the resulting device. The experimentally determined E_0 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_0 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_0 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* $\langle\varepsilon\rangle=\langle\varepsilon_1\rangle+i\langle\varepsilon_2\rangle$ spectra of CZTSe determined by SE in the temperature range of 50 to 350 K, with the primary goal of studying the temperature

* Corresponding author.
E-mail address: sukgeun.choi@nrel.gov (S.G. Choi).

http://dx.doi.org/10.1016/j.solmat.2014.07.039
0927-0248/© 2014 Elsevier B.V. All rights reserved.

dependence of E_0 for CZTSe. Our $\langle\varepsilon\rangle$ data clearly show the fundamental band-gap E_0(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_0(A,B) and its spin–orbit splitting component E_0(C) that are currently lacking in the literature. The observed relatively weak dependencies of the E_0(A, B) and E_0(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 $CuInGaSe_2$ 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_0 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_0. 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

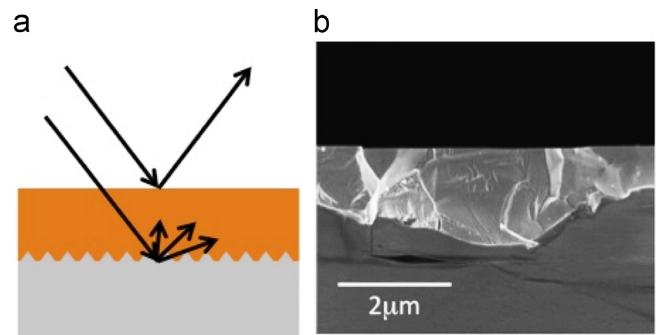


Fig. 1. (a) Schematic and (b) cross-sectional scanning electron micrograph of CZTSe thin film grown on roughened glass surface. The probing light reaches the interface between the film and substrate and is scattered in random directions. The resulting CZTSe thin film can be regarded as a *pseudo-bulk* material. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

complexities in the substrate including inhomogeneity and anisotropic nature. As a result, the extracted E_0 value may be affected by the chosen model parameters, and accurate determination of the film's E_0 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. Fig. 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.

Fig. 2(a) and (b) presents the real and imaginary parts of the $\langle\varepsilon\rangle$ 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_0 of CZTSe at around 1 eV clearly visible in the $\langle\varepsilon_2\rangle$ spectra without need for multilayer modeling. The E_0 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_0 energy may be determined with a large uncertainty.

To obtain the E_0 energy more accurately, we numerically calculated the second-energy-derivative $d^2\langle\varepsilon\rangle/dE^2$ 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.

Download English Version:

https://daneshyari.com/en/article/6535587

Download Persian Version:

https://daneshyari.com/article/6535587

Daneshyari.com