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Published in:
Applied Physics Letters

Link to article, DOI: 10.1063/1.4990657

Publication date: 2017

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
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Citation: Appl. Phys. Lett. 110, 261105 (2017); doi: 10.1063/1.4990657
View online: http://dx.doi.org/10.1063/1.4990657
View Table of Contents: http://aip.scitation.org/toc/apl/110/26
Published by the American Institute of Physics

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Temperature dependent photoreflectance study of Cu$_2$SnS$_3$ thin films produced by pulsed laser deposition

T. Raadik,1, a) M. Grossberg,1 J. Krustok,1 M. Kauk-Kuusik,1 A. Crovetto,2 R. Bolt Ettlinger,3 O. Hansen,2 and J. Schou3

1Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
2DTU Nanotech, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
3DTU Fotonik, Technical University of Denmark, DK-4000 Roskilde, Denmark

(Received 27 April 2017; accepted 15 June 2017; published online 28 June 2017)

The energy band structure of Cu$_2$SnS$_3$ (CTS) thin films fabricated by pulsed laser deposition was studied by photoreflectance spectroscopy (PR). The temperature-dependent PR spectra were measured in the range of $T = 10$–150 K. According to the Raman scattering analysis, the monoclinic crystal structure (C1c1) prevails in the studied CTS thin film; however, a weak contribution from cubic CTS (F-43m) was also detected. The PR spectra revealed the valence band splitting of CTS. Optical transitions at $E_A = 0.92$ eV, $E_B = 1.04$ eV, and $E_C = 1.08$ eV were found for monoclinic CTS at low-temperature ($T = 10$ K). Additional optical transition was detected at $E_A^* = 0.94$ eV, and it was attributed to the low-temperature band gap of cubic CTS. All the identified optical transition energies showed a blueshift with increasing temperature, and the temperature coefficient $dE/dT$ was about 0.1 meV/K. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4990657]

There is a continuous search for alternative absorber materials with an excellent environmental profile for highly efficient photovoltaics. One possible candidate is Cu$_2$SnS$_3$ (CTS) that is a direct-bandgap p-type semiconductor with a high absorption coefficient ($10^5$ cm$^{-1}$) consisting of abundantly available and non-toxic elements. The best solar cell efficiency obtained from monoclinic CTS is 4.63%.1

Cu$_2$SnS$_3$ has been reported to crystallize in three different polymorphs: cubic (F-43m),2,3 tetragonal (I-42m),2,4 and monoclinic (C1c1)5–8 depending on the synthesis temperature where higher temperature leads to a higher degree of symmetry of the unit cell. These polymorphs are barely distinguishable by XRD, whereas Raman spectroscopy has been proved to be more sensitive for determining the phase composition of CTS. It has been shown that CTS synthesized at temperatures below 500–550 °C adopts a cubic or a tetragonal crystal structure, while at higher temperatures, a monoclinic structure is obtained.2,5,9 Additionally, other groups have mainly observed the monoclinic phase at 520–570 °C.7,10,11 but it has also been reported at lower temperatures,9 and the exact temperature might depend on the state of the precursors and the details of the annealing system. Monoclinic CTS absorbers for solar cells have to be grown Cu-poor to avoid alloying with metallic Cu$_3$SnS$_4$,12 and at the same time, the Sn-rich composition may lead to the formation of Cu$_2$Sn$_2$S$_5$.13

The theoretical density functional theory (DFT) calculations predict a triple optical absorption onset for monoclinic CTS,10,14 indicating a valence band splitting. From the DFT calculations, de Wild et al.10 found the theoretical bandgap value of 0.76 eV for monoclinic CTS and the valence band splitting at the $\Gamma$-point between the topmost and the second valence band of $\Delta_I = 0.10$ eV and between the topmost and the third valence band of $\Delta_2 = 0.15$ eV. Experimentally obtained results, calculated from the absorption spectrum, were slightly different. The room temperature bandgap energy value for monoclinic CTS was found to be $E_A = 0.96$ eV, whereas the onset between the main and the second and third uppermost valence bands of $\Delta_I = 0.11$ eV and $\Delta_2 = 0.16$ eV, respectively, is in good accordance with theoretical calculations. Theoretical calculations by using the DFT method of the CTS band structure have also been done by Crovetto et al.14 They reported a double absorption onset in monoclinic CTS and showed that the double onset is related to the intrinsic nature of this compound and not to other CTS phases or compounds. They found a theoretical bandgap value of $E_A = 0.83$ eV for monoclinic CTS and the splitting between the main and the second and third uppermost valence bands of $\Delta_I = 0.12$ eV and $\Delta_2 = 0.16$ eV, respectively. These values are in good accordance with the results obtained by de Wild.10 A similar bandgap value of $E_A = 0.84$ eV, found from theoretical hybrid nonlocal exchange-correlation functional (HSE) calculations, has been reported also by Zhai et al.15 Crovetto et al.14 have also reported the experimental values of optical transition energies determined from absorption spectra at room temperature. Their results showed the bandgap energy $E_A = 0.91$ eV and the second optical transition at 0.99 eV, which is related to $E_B$ transition, while the theoretically predicted third transition $E_C$ was not seen in this study. Similar to de Wild's results, theoretical transition energies calculated by Crovetto et al.14 are much smaller compared with experimental results. As it was mentioned before, CTS has three different polymorphs: besides monoclinic, there are also a cubic and a tetragonal crystal structure that have bandgap energy values higher than monoclinic CTS. Fernandes et al.16 have reported an experimental bandgap value of $E_A^* = 0.96$ eV for cubic CTS and $E_A^* = 1.35$ eV for tetragonal CTS. On the other hand, Guan et al.3 have found bandgap energies of...
The photoreflectance spectrum measured at 10 K together with fittings is shown in Fig. 2. The three derivative-like features corresponding to the multiple optical transitions of CTS that result from the band gap and valence band splittings are clearly visible in the reflectance spectrum. A weak feature at around 0.94 eV was also detected. Each PR spectrum has been analyzed by the low-field line-shape function with a third derivative functional form, developed by Aspnes:23

\[
\Delta R/R = \sum_{j=1}^{n} Re \left[ A_j e^{i\varphi_j} (E - E_{g,j} - i\Gamma_j)^{-m} \right],
\]

where \( E \) is the photon energy and \( A_j \), \( \varphi_j \), \( E_{g,j} \), and \( \Gamma_j \) are the amplitude, phase, optical transition energy, and broadening parameter of the spectrum of the \( j \)th structure, while \( n \) is the number of critical points, in our case 4. The exponent \( m \) depends on the type of the critical point, and determining its proper value is of particular importance in analyzing PR spectra. \( m = 2.5 \), corresponding to a three-dimensional critical point, was used for the fitting of all PR spectra. In order
to study the temperature dependencies of the observed optical transitions, PR measurements were performed in the temperature range of $T = 10–150\,\text{K}$.

The detailed fitting with Eq. (1) revealed four optical transitions at $E_A = 0.92\,\text{eV}$, $E_B = 1.04\,\text{eV}$, $E_C = 1.08\,\text{eV}$, and $E_A^C = 0.94\,\text{eV}$. The latter optical transition $E_A^C$ is attributed to the bandgap energy of cubic CTS since the Raman spectra revealed the presence of the cubic CTS phase in the studied film. Indeed, Fernandes et al.\textsuperscript{16} have found that the cubic phase of CTS has a bandgap of $E_A^C = 0.96\,\text{eV}$. A slightly higher value of $E_A^C = 0.98\,\text{eV}$ has been reported by Zhai et al.\textsuperscript{15} According to the literature, we can attribute $E_A$, $E_B$, and $E_C$ to the bandgap and valence band splitting of the monoclinic CTS, and the band structure can be seen in Fig. 3. Experimentally determined offsets between optical transition energies $E_A$, $E_B$, and $E_C$ were $\Delta_1 = 0.12\,\text{eV}$ and $\Delta_2 = 0.16\,\text{eV}$, and they are in good accordance with the results of the theoretical calculations.\textsuperscript{10,14}

Interestingly, we detected a shift of the PR spectrum towards higher energies with increasing temperature, indicating the widening of the band gap of CTS in the range of $T = 10–130\,\text{K}$, as can be seen in Fig. 4. Measurements at higher temperatures ($T > 150\,\text{K}$) were not possible due to the low PR signal. The bandgap widening with increasing temperature is not very common among the semiconductor materials; however, a similar behavior at low temperatures has also been detected for example in Ag containing ternaries,\textsuperscript{18} black phosphorus,\textsuperscript{24} some chalcogenides [CuInS$_2$,\textsuperscript{25} CuInSe$_2$,\textsuperscript{26} and CuGaSe$_2$\textsuperscript{26}], and hybrid perovskites.\textsuperscript{27} The blueshift of the free exciton PL band of CTS with increasing temperature was also witnessed by Aihara et al.\textsuperscript{7,8} The observed widening of the energy gap appears to be the result of the competition between the thermal expansion and the electron-phonon interaction.\textsuperscript{25} For example, the thermal expansion coefficient at low temperatures can become negative due to the reduction in the unit cell volume, causing a blueshift of bandgap with increasing temperature.\textsuperscript{28} This was seen for example in CuBr by Lewonczuk et al.\textsuperscript{29} However, the origin of the blueshift of the bandgap energy of CTS is not yet clarified and needs to be studied further.

In conclusion, a photoreflectance study of a CTS thin film grown by PLD was performed in the temperature range from 10 to 150 K. From the PR spectra, three low-temperature ($T = 10\,\text{K}$) optical transitions of monoclinic CTS, $E_A$, $E_B$ and $E_C$, were determined. An additional optical transition $E_A^C$ was attributed to the band gap of cubic CTS. All the identified optical transition energies showed the blueshift with increasing temperature, and the temperature coefficient was $\sim 0.1\,\text{meV/K}$.

This work was supported by the institutional research funding project IUT 19–28 of the Estonian Ministry of Education and Research, by the European Union through the European Regional Development Fund, Project TK141, by FP7 project CHEETAH, EC Grant Agreement No. 609788, and a grant from the Danish Council for Strategic Research.


