In-depth resolved Raman scattering analysis for the identification of secondary phases: Characterization of Cu$_2$ZnSnS$_4$ layers for solar cell applications


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This work reports the in-depth resolved Raman scattering analysis with different excitation wavelengths of Cu$_2$ZnSnS$_4$ layers. Secondary phases constitute a central problem in this material, particularly since they cannot be distinguished by x-ray diffraction. Raman spectra measured with 325 nm excitation light after sputtering the layers to different depths show peaks that are not detectable by excitation in the visible. These are identified with Cu$_3$SnS$_4$ modes at the surface region while spectra measured close to the back region show peaks from ZnS and MoS$_2$. Observation of ZnS is enhanced by resonant excitation conditions achieved when working with UV excitation.

Primary phases formed at the surface of the layers were chemically etched in a KCN aqueous solution during 20 s. Electron probe microscopy measurements performed in these layers give an overall Cu/(Zn+Sn) content ratio about 0.97, and an overall Zn/Sn content ratio about 0.95. Preliminary characterization of the layers by grazing incidence XRD measurements show different peaks that have been assigned to the kesterite structure of Cu$_2$ZnSnS$_4$ using ICSD card 01-075-181905-3.$^{*}$ Additional contributions at higher frequencies centered at about 96 and 166 cm$^{-1}$ that are identified with the main vibrational A$_1$ symmetry modes from CZTS. The spectra also show weaker peaks at about 96 and 166 cm$^{-1}$ (not shown in the figure) that are identified with E and/or B symmetry CZTS modes. In addition, fitting of the spectra with Lorentzian curves shows a series of Raman spectra after sputtering the sample with the Ar$^+$ beam from the AES system. To minimize damage in the sputtered region the energy of the Ar$^+$ beam during ion sputtering was kept below 5 keV. The estimated sputter rate is about 50 nm/min.

Figure 1 shows the series of Raman spectra measured at different depths from the CZTS layer using 532.5 nm illumination. As shown, the spectra are characterized by the presence of two main peaks at about 286 and 337 cm$^{-1}$, that are identified with the main vibrational A$_1$ symmetry modes from CZTS. The spectra also show weaker peaks at about 96 and 166 cm$^{-1}$ (not shown in the figure) that are identified with E and/or B symmetry CZTS modes. In addition, fitting of the spectra with Lorentzian curves shows two additional contributions at higher frequencies centered at about 352 and 370 cm$^{-1}$. Assignment of the contribution at about 352 cm$^{-1}$ is not clear; some authors have reported a CZTS vibrational mode at this frequency. On the other hand, this also coincides with the frequency of vibrational

Secondary phases constitute a serious problem for numerous advanced compound semiconductors. Among them are kesterite semiconductors Cu$_2$ZnSnS$_4$ (CZTS) e, which are of interest as absorbers in thin film solar cells. For these semiconductors secondary phases are a particularly serious problem because they are likely to occur since the existence region of single phase kesterite was shown experimentally and theoretically to be rather small. Furthermore, some of the major secondary phases, like ZnS(e) and ternary Cu–Sn–S(e) phases cannot be distinguished by x-ray diffraction (XRD). Here we demonstrate that Raman spectroscopy can distinguish these secondary phases, if using excitation conditions that allow the existence of resonant excitation of the corresponding vibrational modes.

In this work, 1.5 μm thick CZTS layers were grown on Mo coated glass substrates by electrodeposition of metal precursors followed by a sulphurization step in a tube furnace at 550 °C during 2 h. Details on the preparation of the layers are given in Ref. 16. After sulphurization, Cu binary secondary phases formed at the surface of the layers were chemically etched in a KCN aqueous solution during 20 s. Electron probe microscopy measurements performed in these layers give an overall Cu/(Zn+Sn) content ratio about 0.97, and an overall Zn/Sn content ratio about 0.95. Preliminary characterization of the layers by grazing incidence XRD measurements show different peaks that have been assigned to the kesterite structure of Cu$_2$ZnSnS$_4$ using ICSD card 01-075-181905-3.

To clarify the presence of secondary phases in these layers, Raman microprobe measurements were performed with a LabRam HR800-UV Horiba-Jobin Yvon spectrometer coupled with an Olympus metallographic microscope. Backscattering measurements were made with two different excitation wavelengths (532.5 and 325 nm) by focusing the laser spot onto the surface of the layers. In both cases, excitation power was kept below 40 μW in order to avoid presence of thermal effects in the spectra. Measurements with the 532.5 nm excitation line were made because of the optimal Raman scattering efficiency of kesterite compounds at these excitation conditions. In addition, in order to enhance detection sensitivity to the potential presence of ZnS phases, Raman scattering measurements were also done with an excitation wavelength relatively close to the band gap of this compound [3.84 eV (Ref. 17)], aiming at resonant excitation conditions.

In-depth chemical composition profiles were obtained by means of Auger electron spectroscopy (AES) using a Phi 670 scanning Auger nanoprobe. Combined in-depth resolved Raman/AES measurements were made by acquiring sequentially a series of Raman spectra after sputtering the sample with the Ar$^+$ beam from the AES system. To minimize damage in the sputtered region the energy of the Ar$^+$ beam during ion sputtering was kept below 5 keV. The estimated sputter rate is about 50 nm/min.

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modes reported for Cu$_2$SnS$_3$, Cu$_3$SnS$_4$, and ZnS compounds. Identification of this mode with the Cu$_2$SnS$_3$ phase is however doubtful because of the lack of an additional peak at about 290 cm$^{-1}$ characteristic of this compound, as was shown by Raman measurement of reference Cu$_2$SnS$_3$ samples grown by the same method. Identification of the mode with the Cu$_3$SnS$_4$ phase is also doubtful because of the absence in the experimental spectra of a peak at about 317 cm$^{-1}$ that has been reported as the main vibrational mode from this compound. Finally, the peak at about 370 cm$^{-1}$ agrees with a CZTS characteristic mode reported for Cu$_2$Sn$_2$S$_5$ samples grown by the same method. Identification of this mode with the Cu$_2$Sn$_2$S$_5$ phase is also doubtful because of the lack of a second order band from ZnS. These measurements suggest the existence of a higher Raman efficiency of this ternary secondary phase when exciting within the UV spectral range.

These measurements demonstrate the presence of a dominant CZTS phase through the whole thickness of the layers. Spectra measured at higher depths (corresponding to sputter times ≥25 min) show additional dominant peaks at about 380 and 408 cm$^{-1}$ that are due to the formation of an interfacial MoS$_2$ phase at the interface region with the Mo coated substrate. Fitting of the main CZTS modes with Lorentzian curves has allowed us to observe the existence of a small redshift (on the order of 0.1 cm$^{-1}$) of the peaks toward lower frequencies that increases with the sputter time. This could be related to the existence of a slight gradient in strain or crystal quality in the layers. Nevertheless, the small amount of this shift points out a relatively high in-depth homogeneity of the CZTS phase through the whole thickness of the investigated layers.

Figure 2 shows the corresponding spectra measured in the same sample with UV excitation conditions. In this case, the spectra measured at the surface region of the sample (sputter time ≈10 min) are characterized by the main CZTS modes at 286 and 337 cm$^{-1}$, and we observe an additional peak at about 315 cm$^{-1}$. The frequency of this peak is close to the main vibrational mode from the orthorhombic Cu$_2$SnS$_4$ phase reported at about 318 cm$^{-1}$. Also, a characteristic peak at about 348 cm$^{-1}$, which could explain the increase in the intensity of the contribution at the 350 cm$^{-1}$ region in these spectra in relation to those measured at 532.5 nm excitation conditions. These measurements suggest the existence of a higher Raman efficiency of this ternary secondary phase when exciting within the UV spectral range.

In addition, at higher depths (sputter time between 15 and 25 min) we observe a strong increase in the intensity of the mode at about 350 cm$^{-1}$ that becomes the dominant peak in the spectra. This is also accompanied by the appearance of a band at about 700 cm$^{-1}$. This behavior is interpreted as due to the existence of resonant excitation conditions that lead to a sharp increase in the efficiency of the main vibrational mode from ZnS at this frequency. This increase explains also the appearance of the peak at about 700 cm$^{-1}$, as shown in the inset of the figure, that has been identified with a second order band from ZnS. These measurements provide a direct experimental evidence on the formation of a ZnS secondary phase.

As for the 532.5 nm excited spectra, the UV excited spectra measured at higher depths (sputter time about 30 min) show again vibrational modes at about 380 and 408 cm$^{-1}$ characteristic of the MoS$_2$ interfacial phase. Working with UV excitation conditions leads also to the observation of an additional peak at about 286 cm$^{-1}$ that is close to the frequency of an E symmetry mode characteristic of MoS$_2$ reported at about 287 cm$^{-1}$.

Finally, in Fig. 3 are plotted the AES elemental profiles measured in these layers. These measurements suggest the existence of similar Zn and Sn profiles, taking into account
their experimental uncertainty. In addition, the samples are characterized by the existence of a S rich region close to the back interface with the Mo coated substrate, and above the MoS2 interface region. This correlates with the region where ZnS resonant peaks have the highest intensity in the Raman spectra measured under UV excitation conditions. This suggests that the formation of the ZnS secondary phase is favored at S excess conditions, being in this region the S content higher than that corresponding to the stoichiometric composition of the main CZTS phase. These data point out the need for an optimization of the sulphurizing step in order to ensure a more homogeneous distribution of S in the layers. This gives interest to the further analysis of the processes involved in the annealing of the layers, as well as of their dependence on the structure of the as-deposited precursors (stacked elemental layers or coelectrodeposited metallic alloy).

In summary, these experimental measurements corroborate the strong potential of Raman scattering based techniques for successful detection and in-depth resolved analysis of secondary phases. In particular, we demonstrate that we can detect secondary phases which cannot be distinguished by XRD based techniques. The use of resonant conditions for the Raman spectroscopy is essential for the reliable detection of these secondary phases, whereas Raman spectroscopy under nonresonant excitation conditions at the visible spectral range do not allow identifying their presence because of the very low Raman efficiency characteristic of the corresponding modes at this excitation spectral range.

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