Spatially-resolved high-power high-temperature Raman spectroscopy as an effective tool for probing the microscopic structural variations in complex alloys: CZTSe as an example

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Abstract — We show that nominally similar CZTSe films may differ significantly in their microscopic structures that cannot be easily revealed by applying conventional characterization tools, including conventional Raman. CZTSe films prepared by sputtering and co-evaporation are examined in both lateral and depth direction to demonstrate the effectiveness of this spectroscopy method.

I. INTRODUCTION

Different fabrication techniques represent different paths to the efficiency limit set by Shockley–Queisser limit. Even two techniques yield comparable efficiencies, the absorber layers could be different in their microscopic structures. It is of great interest to know the differences. TEM is commonly viewed as the most reliable and accurate technique for structural analysis, but it is destructive and inefficient. Raman spectroscopy is an effective tool for chemical composition and structural analyses of materials. It is typically used under the assumption that the probe light intensity is sufficiently low such that no structural change has been induced by the perturbation. In this work, we use “high power (HP)” or “high excitation density” Raman spectroscopy involving a tightly focused CW laser with a power density that is just high enough to introduce a local structural change, and probe the change using “low power (LP)” Raman spectroscopy. Performing spatially resolved Raman mapping on an as-grown material can already reveal composition and/or structural variations in the sample. However, the application of the HP Raman spectroscopy can reveal some subtle but important structural differences in two samples that might otherwise appear to be indistinguishable under the normal probes, such as LP Raman, PL, XRD, and device characteristic. HP Raman spectroscopy, in conjunction with the high spatial resolution of the confocal optics, is a very powerful approach for probing the structural inhomogeneity, in particular in a complex alloy like Cu2ZnSnSe4 (CZTSe), with much greater efficiency and/or sensitivity than TEM and other laser spectroscopy techniques.

II. EXPERIMENTAL DETAILS

All Raman measurements were performed with a Horiba Jobin Yvon HR800 confocal Raman system using a 532 nm laser. The room temperature measurement was carried out with a 100x objective lens with NA = 0.9. The diffraction limit laser spot size is 0.76 μm, and the spatial resolution of the measurement is about half of the laser spot size. A 50x long working distance lens with NA = 0.5, was used in high temperature Raman tests. Sample was heated by Linkam TS1500 heating system with temperature control accuracy of 1 °C.

Two bare CZTSe film samples were studied. CZTSe_97 (S1) was prepared by selenizing the metal stacks which composed of 300 nm Mo, 130 nm Zn, 155 nm Cu and 180 nm Sn sputtered on an Ashai PV 200 glass substrate. The film compositions are \([\text{Zn}] / [\text{Sn}] \approx 1.25\) and \([\text{Cu}] / ([\text{Zn}]+[\text{Sn}]) \approx 0.85\), and the thickness is slightly higher than 1 μm. A device with nominally similar absorber was measured with ~5% efficiency. M3599_12 (S2) was grown by a vacuum co-evaporation method on a soda lime glass substrate, with 1 μm sputtered Mo back contact and 150 Å e-beam evaporated NaF precursor. The film thickness and composition of S2 are 1.49 μm, \([\text{Zn}] / [\text{Sn}] \approx 1.32\) and \([\text{Cu}] / ([\text{Zn}]+[\text{Sn}]) \approx 0.82\). A device with the nominally same absorber had an efficiency of ~8%.

III. RESULTS AND DSSCUSSIONS

A. Raman Studies from Front Surface

In Fig. 1 plotted in dash curves, typical LP Rama spectra from two CZTSe samples were obtained from their front surface with 0.147 mW (3.5 x 10^4 W/cm^2) laser power. Both CZTSe films showed two intense Raman peaks 195 – 196 cm^-1, 172 – 173 cm^-1, and a weak peak at 232 – 233 cm^-1, which are very close to the single crystal Raman scattering peaks at 196, 173 and 231 cm^-1 [1]. Additional peaks at 221.8, 222.7, 243.9 – 244.4, 249.2 and 251– 252.7 cm^-1 were also observed. Among them, the 221–223 cm^-1 peak is believed to be a TO Raman mode from kesterite structure based on calculations [2-4]. 244–245 cm^-1 was also reported to be CZTSe related both experimentally and theoretically [5-7]. The presence of secondary phase Cu2SnSe3 contributes to weak peaks located near 251 cm^-1 [1]. ZnSe was observed at 252.7 cm^-1. Amorphous selenium (a-Se) was reported to display a Raman feature at ~ 250 cm^-1 and a shoulder at ~ 235 cm^-1 when crystallized trigonal Se (t-Se)
exists in a-Se [8]. It is also possible that selenium is present in CZTSe films since they were fabricated in a Se-rich condition. The origin of the broad band ranging from 380 to 390 cm⁻¹ is still unclear.

High laser power effect on CZTSe Raman scattering was observed by comparing Raman spectra taken at the same spot before and after HP illumination. For each sample, after taking the Raman spectrum shown in red, the same spot was illuminated with 2.47 mW (5.9 x 10⁵ W/cm²) for 100 seconds, then the Raman spectrum was re-measured with 0.146 mW under the same conditions. After the HP illumination, the illuminated spot showed some color change, becoming lighter under optical microscope, but no apparent ablation. The results for the two samples are shown in Fig. 1 green curves. The two main CZTSe peak at 195 – 196 cm⁻¹ and 171 – 172 cm⁻¹ experienced not only intensity reduction, but also red shift in both samples. Besides, some new peaks appeared after HP illumination. In Fig. 1 (a), a new Raman peak at 242 cm⁻¹ was observed from S1. This 242 cm⁻¹ peak matches A₁g Raman mode of MoSe₂ [9]. For S2 in Fig. 1 (b), new peak appeared at 234.7 cm⁻¹ which is close to the 235 cm⁻¹ shoulder from crystallized trigonal Se (t-Se) observed in a-Se [8].

The laser power was further increased to 4.5 mW (1.1 x 10⁶ W/cm²) to illuminate the same spot for 36 seconds. Raman data were collected again with 0.147 mW power. As shown in Fig. 3 (a), the intensity of 193 cm⁻¹ peak of S1 is only 10% of its original value before high power illumination, and the 172 cm⁻¹ mode became a weak shoulder from 168 cm⁻¹ to 178 cm⁻¹. In addition, a sharp and strong peak appears at 241.7 cm⁻¹, which is enhanced from the 242.2 cm⁻¹ peak in Fig. 1 (a). Interestingly, the main CZTSe peak intensity only dropped by a factor of four, and the ~ 172 cm⁻¹ CZTSe peak remains sharp in S2 after 4.5 mW illumination. Furthermore, the 242 cm⁻¹ peak do not appear as shown in Fig. 2(b). Obviously, HP illumination brought qualitatively different changes to the two samples. The contrast between S1 and S2 suggests that there are some subtle microscopic differences between the two samples.

2D Raman mapping was performed to examine the spatial extension of the local heating effect caused by the high power illumination on CZTSe sample surface. One random spot from each sample surface was first illuminated by 2.47 mW for 100s, Raman mapping was then acquired from a 5x5 μm (Fig. 3) or 8x8 μm (Fig. 4) square centered at the illuminated spot with 0.147 mW laser power. For S1, in addition to the CZTSe mode at 196 cm⁻¹, another peak ~261 cm⁻¹ was also observed as a ring near the illuminated site. For S2, on the other hand, 2.47 mW laser illumination only affected a range ~1.5 μm circle, Fig. 4(a), and did not generate a Cu₂Se₅ ring, Fig. 4(b). The difference between S1 and S2 seems to suggest that the two nominally similar films might have different thermal conductivities, and also that CZTSe absorber prepared by sputtering method is more sensitive to high power illumination than film fabricated by co-evaporation method.
Raman spectra were measured from cleaved edge with laser beam focused to different depths of the sample: Mo layer, Mo-CZTSe boundary, body of film, film-air boundary and air (when the beam was just moved off the edge of the front surface). Because of the limitation of the laser spot size, these measurements can only reveal the qualitative changes. Measured at lower power condition (0.147 mW) from the cleaved edge, one can clearly see the variation of the spectral features with film depth in Fig. 5. For S1, MoSe₂ is dominant component at the substrate-film boundary with Raman modes at 169, 242, 286 and 351 cm⁻¹ in S1. The mode ~ 196 cm⁻¹ appears in both Mo and CZTSe layers, although substantially weaker in the Mo region. When moving toward the front surface, the MoSe₂ related peaks gradually diminish, whereas the CZTSe peaks at 196 cm⁻¹ and 172 cm⁻¹ grow. In contrast, no Raman signal from MoSe₂ was observed near the substrate of S2.

The measured cleaved edge spots were then illuminated by 2.47 mW for 100 seconds and Raman spectra from these spots were collected again with 0.147 mW. In addition to red shift, a very weak peak at 262.3 cm⁻¹ was observed when laser moved beyond the CZTSe film. However, No new peak appeared from S2 cleaved edge after being illuminated by 2.47 mW. Increasing the illumination laser power to 4.5 mW for 36 seconds, CuₓSeᵧ peak at 261.5 cm⁻¹ could also be observed from S2 cleaved edge spectra. Besides, a peak at 263.1 cm⁻¹ which is close to CuₓSeᵧ Raman mode showed up in the Raman spectrum from substrate of S1, as shown in Fig. 6. Additionally, many new peaks were detected at its substrate and CZTSe film boundary, such as SnSn peak 185.6 cm⁻¹, ZnSe peak at 202.6 cm⁻¹, and some other peaks at 729.3 cm⁻¹ and 819.0 cm⁻¹ which are very close the molybdenum oxide Raman modes. The result of cleaved edge Raman after high power laser illumination from S1 confirms this process 2CuₓZnSnSeᵧ + Mo → 2CuₓSeᵧ + 2ZnS + 2SnSe + MoSe₂/predicted in Ref. [10] with co-existence of MoSe₂, ZnSe, SnSe and CuₓSeᵧ near the substrate and film boundary. However, in Fig. 6(b), only secondary phases CuₓSnSeᵧ/a-Se and CuₓSeᵧ but no ZnSe or MoSe₂ was found. These observations again indicate the microscopic structure of the polycrystalline CZTSe film could vary substantially with deposition method.

IV. CONCLUSIONS

High power micro-Raman studies were performed on two CZTSe samples: sputtered and co-evaporated film. In general, HP illumination brought more changes to sputtered film, not only in the CZTSe Raman peaks but also in the secondary phases, which suggests that films prepared by the sputtering methods is structurally less robust than that of films fabricated by the co-evaporation method. HP Raman study is demonstrated as an effective approach to examine the microscopic structural variations of the complex alloys like CZTSe that might otherwise appear to be similar in their simple room temperature Raman spectra and device performance.

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REFERENCE


