## Chapter 7

# Application of spatially resolved spectroscopy characterization techniques on Cu<sub>2</sub>ZnSnSe<sub>4</sub> solar cells

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## 7.1 Raman spectroscopy and CZTSe solar cells

## 7.1.1 Raman spectroscopy

Raman spectroscopy is named after C.V. Raman who observed the Raman effect for the first time in 1928. Today, Raman spectroscopy is widely used in various fields—from fundamental research to applied solutions. This spectroscopic technique takes advantage of light interaction with vibrational and rotational states of materials.

When light shines on a sample and interacts with the material, the dominant scattering is elastic scattering that does not involve energy change and is referred to as Rayleigh scattering. However, it is also possible that the incident light interacts with the material in such a way that the energy is either transferred to or received from the sample, resulting in an energy change of scattered photons or a frequency shift of the scattered light. Such inelastic scattering is the so-called Raman scattering. Similar to Rayleigh scattering, the material in Raman scattering also needs to be polarizable because the incident photon interacts with the electric dipoles in the material. In classic terms, the interaction can be viewed as a perturbation to the material's polarization field [1]. From a quantum mechanics perspective, the incident photons can excite the vibrational modes of the material; in this way, photons give up energy and are scattered with a lower (red-shifted) frequency than that of Rayleigh-scattered light. A spectral analysis of the scattered light can reveal light signals at frequencies different from the incident light, and the lower-frequency lines are referred to as Stokes Raman scattering. Alternatively, if the system is already in a vibrational excited state, it is possible that the vibrational energy can be transferred to the incident photon, leading to a blue-shifted frequency that is greater than the incident frequency, referred to as anti-Stokes Raman scattering. Figure 7.1

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Figure 7.1 Energy-level diagram and relative locations in frequency of Rayleigh, Stokes, and anti-Stokes scattering: (a) energy diagram and (b) Raman and Rayleigh lines

(a) shows the energy-level diagram involved in Rayleigh and Raman scattering, and Figure 7.1(b) shows the relative locations of three different scattering lines in frequency domain. In most cases, the probability of a system in the vibrational excited state is much lower than in the ground state. As a result, the probability of the anti-Stokes scattering is usually much less than that of the Stokes scattering. Usually, Stokes scattering is studied in most applications.

The frequency shift or Raman shift is typically measured in wavenumber, with a unit of inverse length. Photon energy is inversely proportional to wavelength, so the energy change can be converted to a shift in wavenumber in Raman spectrum using the following equation:

$$\Delta \omega = \frac{1}{\lambda_0} - \frac{1}{\lambda}$$

where  $\Delta \omega$  is the Raman shift in wavenumber,  $\lambda_0$  is the incident wavelength, and  $\lambda$  is the scattered wavelength. Usually, the unit chosen for the Raman shift is inverse centimeter, cm<sup>-1</sup>, and the wavelength in the above equation is in centimeter.

Raman scattering originates from a change in the polarizability of the material due to an interaction of light with the material, which corresponds to specific energy transitions. As a result, Raman spectroscopy is a form of vibrational spectroscopy. The energy of the vibrational mode is determined by many aspects: crystal structure, atomic mass, iconicity, bonding, and so on, all of which are directly related to the specific characteristics of the material. By probing individual vibration modes, Raman spectroscopy can be used to identify the structure and composition because it provides a "fingerprint" of the material being measured. Raman spectroscopy is a very important tool in semiconductor research and characterization.

By using light interaction with a sample, Raman spectroscopy involves only a laser illuminating a sample and then collecting the scattered photons, which offers advantages such as being nondestructive, requiring no sample preparation, and providing a fast measurement. Since Raman spectroscopy is noncontact and non-destructive (if the power is sufficiently low), it is possible to make repeated measurement as well as correlative analyses by applying other techniques.

## 7.1.2 CZTSe solar cells

The quaternary compounds  $Cu_2ZnSnS_4$  (CZTS) and  $Cu_2ZnSnSe_4$  (CZTSe) are promising thin-film absorber materials by substituting zinc and tin for indium and gallium in a  $CuInGaS_2$  (CIGS) absorber. The quaternary compound has three types of crystal structures-kesterite, stannite, and premixed Cu-Au (PMCA)-with kesterite being the main structure used for photovoltaic (PV) application. Although first made in 1967 [2], scientists did discover the PV effect of CZTS [3] until 1988. CZTS, as a p-type semiconductor, has a high absorption coefficient for visible light. The direct optical bandgap is 1.45 eV, which matches the best semiconductor bandgap value for PV application according to the Shockley-Queisser limit [4]. Thereafter, major effort was devoted to fabricate solar devices with these materials, and the efficiencies of CZT(S,Se) cells have continuously increased over the past 20 years. The first CZTS cell was fabricated in 1996 with only 0.66% efficiency and open-circuit voltage ( $V_{oc}$ ) of 400 mV [5]. The efficiency was improved to 2.3% and  $V_{\rm oc}$  to 470 mV for both CZTS and CZTSe cells the next year [6]. By 2008, CZTS cell efficiency improved to 6.7% [7]. In 2010, 7.2% and 9.6% CZTSSe cells were fabricated by different methods [8,9]. Also the first CZTSSe cell with over 10% efficiency was demonstrated in 2011 [10]. In 2013, the highest energy efficiency obtained from a CZTSSe solar cell was 12.6% [11]. Unfortunately, the record efficiency remains the same till today. This situation is largely due to the emergence of a new PV material CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> that has shown unprecedented rapid improvement in efficiency, currently reaching 23.7%, which has led to the diversion of the resources from areas like CZT(S,Se) to the new area.

Although CZT(S,Se) is not a PV material of broad interest currently, in this chapter we use it as a prototype system to illustrate how multiple spatially resolved optoelectronic characterization techniques when applied correlatively can lead to more comprehensive insights to the material properties and device performance than applied them independently. The methodologies and practices can be easily adopted for other PV materials and devices and in general (opto)electronic materials and devices. With this finding, we hope that the unique insights obtained through our studies could benefit those researchers who have not given up on CZT(S,Se).

## 7.2 Spatially resolved Raman spectroscopy in conjunction with laser-beam-induced current/ photoluminescence/reflectance/scanning electron microscope/atomic force microscopy

Laser-beam-induced current (LBIC) is another high-resolution, nondestructive optoelectronic characterization technique. It is used to spatially map device photo-response. In the technique, a laser beam is focused on the solar cell surface and the short-circuit current induced by the laser beam in the solar cell is measured. By scanning the laser beam across the sample or moving the sample with a XY stage, the current values at different spatial points can be translated to a color value and shown as a two-dimensional (2D) LBIC mapping image representing the spatial distribution of the photo-response in the scanned semiconductor region. As a result, electrical defects can be easily visualized. Depending on the laser spot size and scanning step size, the spatial resolution can range from submicron to several hundred micrometers. It is well known that the spatial inhomogeneity in a semiconductor can have a significant effect on the uniformity in the performance of the final optoelectronic device. With micro-LBIC, inhomogeneity at the micron scale can be identified.

Reflection signals are categorized as specular reflection and diffuse reflection according to the surface condition. In a microscopic-scale measurement, a major portion of diffuse reflection as well as specular reflection can be captured simultaneously with the help of an objective lens with high numerical aperture (NA) focused on the sample surface [12].

Integrating and correlating multiple nondestructive spatially resolved techniques is a powerful approach in studying optoelectronic properties of thin-film solar cell materials and devices [12].  $\mu$ -Raman spectroscopy, probing the "fingerprints" of the material structures and compositions, can be used to analyze the chemistry in the sample. Micro-photoluminescence ( $\mu$ -PL) can be used to estimate the bandgap and detect possible defects.  $\mu$ -LBIC can probe the photo-response of the solar cell under different illumination density conditions and visualize the structural defects and the impact of microscale film inhomogeneity at the same time.  $\mu$ -Reflectance offers a more accurate method to estimate the reflectance loss of a rough sample surface, especially comparing the general area with nonuniform regions.



Figure 7.2 Raman and PL spectra from three types of regions: (a) Raman and (b) PL

On a microscopic scale, three distinctly different types of regions-referred to as general area, dark spot, and bright spot-can be observed on a typical CZTSe solar cell under optical microscope with white-light illumination. Figure 7.2(a) and (b) compares typical Raman and PL spectra, respectively, from the three regions measured with a 532-nm laser. In Figure 7.2(a), in addition to the two typical CZTSe Raman modes at 172 and 196  $\text{cm}^{-1}$ , another Raman mode at 303  $\text{cm}^{-1}$  is also observed from all the three regions. This 303 cm<sup>-1</sup> peak is strongly enhanced at both dark and bright spots, in particular, with the appearance of another peak of  $602 \text{ cm}^{-1}$  at the bright spot. These two peaks match, respectively, the first- and second-order longitudinal optical (LO) phonon Raman peaks of CdS. The observation of 1LO and 2LO peaks can be understood as the resonant Raman effect of CdS because the excitation energy of the 532-nm laser (~2.33 eV) is very close to that of the CdS bandgap (2.42 eV). Furthermore, as shown in Figure 7.2(b), both bright and dark spots give rise to a broad PL band at 1.73 eV, which is far above the bandgap of CZTSe (~0.96 eV), presumably associated with defects in the polycrystalline CdS. Therefore, the CdS layer is the thickest at the bright spot and thinnest at the general area. To further study the effect of the microscopic-scale thickness fluctuation of CdS on the device performance, one can perform an array of mutually correlated microscopic characterizations from the same area of the device.

Figure 7.3 shows 2D imaging or mapping of optical microscope, scanning electron microscope (SEM), reflectance, Raman, PL, and LBIC—all acquired approximately from a single 20  $\mu$ m × 20  $\mu$ m area on a CZTSe device with a 100× objective lens (NA = 0.9). Reflectance (Figure 7.3(c)) was obtained with ~18 pW power (~4.4 × 10<sup>-3</sup> W/cm<sup>2</sup>), LBIC (Figure 7.3(f)) with ~2  $\mu$ W power (~4.9 × 10<sup>2</sup> W/cm<sup>2</sup>), and Raman (Figure 7.3(d)) and PL (Figure 7.3(e)) with 200  $\mu$ W power (~4.9 × 10<sup>4</sup> W/cm<sup>2</sup>), all with the 532-nm laser. The optical image (Figure 7.3(a)) reveals a bright region of a few micrometer size near the center and some scattered dark spots, which are identified to be CdS-rich according to its Raman and PL spectroscopy, as shown in Figure 7.2. The SEM image (Figure 7.3(b)) further confirms the variation in surface morphology. The extra height of the bright regions





is estimated to be  $1-1.5 \,\mu\text{m}$  using atomic force microscopy (AFM). An aluminum mirror with its reflectance data provided by the vendor was used as a reference to obtain the reflectance mapping shown in Figure 7.3(c). The reflectance mapping shows that the bright CdS-rich region is much more reflective than the general area, whereas the dark spots are less reflective than the rest of the area-in good agreement with the optical image because both of them result from reflection. Both Raman (monitored at 303 cm<sup>-1</sup>) and PL (monitored at 1.73 eV) clearly reveal stronger signals from the bright region than from the general area, as shown in Figure 7.3(d) and (e). As expected (and observed in Figure 7.3(f)), the CdS-rich regions, including the large bright island and scattered black spots, yield much smaller photocurrent—reduced by as much as a factor of 3—than the general area. Yellow circles in LBIC mapping correlate with the dark spots in the optical images. By comparing Figure 7.3(c) and (f), one can find the general anti-correlation between the reflectance and LBIC mappings. Lower current from the CdS-rich region indicates the potential to optimize the thickness of the CdS layer to further improve device performance.

### 7.3 Secondary-phase identification

Similar to its parent CIGS, CZT(S,Se) also has a narrow region of phase stability in which the device-quality material can be synthesized without major adverse effects of secondary phases. The formation of binary and ternary secondary phases-including  $Zn_xS(Se)$ ,  $Cu_xS(Se)$ ,  $Sn_xS(Se)$ , and  $Cu_xSnS(Se)_v$ —are often observed in CZT(S,Se) films. Usually, film quality, defect formation, and secondary-phase formation are coupled. The presence of these secondary phases has been assumed to contribute to lowering the energy conversion efficiency of the solar cell. For example, Cu-Sn-S clusters could act as recombination centers, resulting in a lower  $V_{OC}$ ;  $Cu_{2-x}S$  could even short the device; and ZnS may reduce the volume of the useful material and absorb the shorter wavelengths and lower external quantum efficiencies (EQEs) when present at the film surface. Achieving a high-quality film requires a higher degree of understanding and control of the CZT(S,Se) phase space. Detection of secondary phases will guide how to improve the growth method for the CZT(S,Se) thin film. Identifying secondary phases using only X-ray diffraction (XRD) in CZT(S,Se) is not as easy as in CIGS because kesterite CZTS shares multiple peaks with cubic ZnS and Cu<sub>2</sub>SnS<sub>3</sub>. Raman spectroscopy is a powerful characterization method to reveal vibrational signatures of CZT(S,Se) and especially of secondary phases.

Two CZTSe samples—one prepared by a sputtering method (S1) and the other by a co-evaporation method (S2)—were measured and results are shown in Figure 7.4. Raman spectroscopy was performed at room temperature with a 147  $\mu$ W (3.5 × 10<sup>4</sup> W/cm<sup>2</sup>) 532-nm laser and 100× lens. Both samples exhibit rather similar Raman features: two intense Raman peaks at 195–196 cm<sup>-1</sup> and 172–173 cm<sup>-1</sup> and a weak peak at 232–233 cm<sup>-1</sup>, which are very close to single-crystal CZTSe Raman peaks at 196, 173, and 231 cm<sup>-1</sup>. Except for the primary CZTSe Raman scattering peaks, additional peaks at 222, 244, and 251 cm<sup>-1</sup> are also observed.



Figure 7.4 Raman spectra of two CZTSe samples measured at 0.147 mW from front surface: (a) S1 and (b) S2

Based on the theoretical calculations, the peak of ~222 cm<sup>-1</sup> is believed to be a transverse-optical (TO) Raman mode in E symmetry from kesterite structure [13–15]. The peak of ~244 cm<sup>-1</sup> was also reported both experimentally and theoretically to be CZTSe-related [16–18]. The peak of ~251.5 cm<sup>-1</sup> is close to the Raman modes of these possible secondary phases: 253 cm<sup>-1</sup> of ZnSe, 251 cm<sup>-1</sup> of Cu<sub>2</sub>SnSe<sub>3</sub>, and ~250 cm<sup>-1</sup> of amorphous selenium (a-Se) [19–23]. The origin of this peak is shown to be a-Se in Section 7.4.

Raman spectroscopy can be performed from the front surface and also from a cleaved edge. By comparing Raman spectra from different positions of the cleaved edge, one can achieve a better understanding of the composition depth profile and the subtle difference between films prepared by different methods. Raman spectra are measured with the laser beam focused to different depths of the sample: Mo layer,

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Figure 7.5 Raman spectra of two CZTSe samples measured from cleaved edge: (a) S1 and (b) S2

Mo/CZTSe boundary, body of film, film/air boundary, and air (when the beam is just moved off the edge of the front surface). Due to the limitation of the laser spot size, these measurements can only reveal the qualitative change. In Figure 7.5, measured at 0.147 mW ( $3.5 \times 10^4$  W/cm<sup>2</sup>) from the cleaved edge, one can clearly see the variation of the spectral feature with film depth. The spectra reveal the evolution of the dominant components from (Mo) substrate to the absorber film. In Figure 7.5(a), only very weak peaks at 169, 196, 241, 286, and 351 cm<sup>-1</sup> are detected on the substrate. Observed close to the molybdenum layer, MoSe<sub>2</sub> is the dominant component at the substrate/film boundary with Raman modes at 169, 242, 286, and 351 cm<sup>-1</sup> in S1. The mode at ~196 cm<sup>-1</sup> appears in both Mo and CZTSe layers,

although substantially weaker in the Mo region. When moving toward the front surface, the MoSe<sub>2</sub>-related peaks gradually diminish, although they remain throughout the film thickness, whereas the CZTSe peaks at 196 and 172 cm<sup>-1</sup> grow. Compared with the results measured from the front surface, one can conclude that MoSe<sub>2</sub> concentrates at the substrate/film boundary and exists throughout the film thickness in this sputtered sample. In contrast, no Raman signals from MoSe<sub>2</sub> are observed near the substrate of S2, as shown in Figure 7.5(b). Only CZTSe Raman modes at 172, 196, and 232 cm<sup>-1</sup> as well as secondary phases such as ternary compound Cu<sub>x</sub>SnSe<sub>y</sub> or a-Se at 250.9 and 235 cm<sup>-1</sup> are observed from S2.

## 7.4 Laser-induced-modification Raman spectroscopy

Transmission electron microscopy (TEM) is generally considered to be a direct probe for the material structure. However, the probing volume of TEM tends to be small—typically on the order of a few tens of nanometers—which places a severe limit on the characterization efficiency when one needs to have macroscopic-scale structural information of an inhomogeneous material. Two better-known laserbased material analysis techniques-laser-induced-breakdown spectroscopy (LIBS) and femtosecond-laser tomography-are destructive and do not offer information on chemical bonding. In contrast, "high power" (HP) Raman spectroscopy, as a special form of laser-induced-modification spectroscopy (LIMS) [24], uses a tightly focused continuous-wave laser with a power density that is just high enough to induce a local structural change but usually without causing major material ablation; it measures the change in Raman features compared with the spectrum before the illumination under "low power" (LP). Performing spatially resolved Raman mapping on an as-grown material can already reveal composition and/or structural variations in the sample. However, the HP Raman spectroscopy can provide additional information beyond that obtainable from the conventional technique. For instance, some structural or chemical fluctuations are too weak to be detected or distinguished in the as-grown sample or between different ones, but they are magnified after being modified by the HP illumination. 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 if they were only subjected to conventional probes, such as Raman spectroscopy, PL, XRD, and device characterization.

S1, S2, and another co-evaporated CZTSe device, S3, are compared. Raman spectra of S1 and S2 are obtained with two powers—32.8  $\mu$ W (7.9 × 10<sup>3</sup> W/cm<sup>2</sup>) and 146  $\mu$ W (3.5 × 10<sup>4</sup> W/cm<sup>2</sup>)—as shown in Figure 7.6, from the same location with no grating movement between the two measurements. The primary CZTSe Raman modes of S1 experience a 0.4 cm<sup>-1</sup> redshift when the laser power is increased. When remeasured with the lower power, the observed redshift is reversible, indicating an elastic change. For S2, no shift is observed with the power change. The slight CZTSe Raman mode redshifts indicate that a small heating effect is introduced for the sputtered sample under 146  $\mu$ W illumination, but the



*Figure 7.6 Raman spectra of the bare CZTSe films measured at 32.8 and 146 μW:* (a) S1 and (b) S2

power level is not high enough to cause irreversible material modification. The comparison suggests some subtle structural difference between the two samples manifested in the difference in thermal conductivity.

Figure 7.7 examines the effects of HP illumination by comparing the LP Raman spectra from the same location at 0.146 mW before and after 100 s illumination at 2.47 mW ( $5.9 \times 10^5$  W/cm<sup>2</sup>) and a further 36 s at 4.5 mW ( $1.1 \times 10^6$  W/cm<sup>2</sup>). After the 2.47-mW illumination, the illuminated spot shows some color change under optical microscope but no apparent ablation. However, the 4.5-mW illumination typically results in some local material ablation. However, for a bulk Si shown in Figure 7.7(f), even illuminated with the full power (about 20 mW,  $4.9 \times 10^6$  W/cm<sup>2</sup>), there is practically no change when returned to the LP condition.

The red curves in Figure 7.7(a)–(c) are typical Raman spectra from the three CZTSe samples measured first at 0.146 mW, and the green and blue curves are the corresponding spectra remeasured after the two higher-power illuminations. All three samples exhibit rather similar Raman features in their initial states. The "mesa-like" band to the right of the 196 cm<sup>-1</sup> peak with multiple weak peaks is compared directly in Figure 7.7(d) among the three samples in their initial states, indicating that there is no significant or distinct difference between the samples prepared differently. As a matter of fact, more variations can be found within one sample, due to composition inhomogeneity [25], as shown in Figure 7.7(e) between different locations in S2. Therefore, it is impractical to use conventional Raman spectroscopy to reliably reveal potential structural variations from sample to sample. The peak of ~251.5 cm<sup>-1</sup> is close to the Raman modes of these possible secondary phases: ZnSe, Cu<sub>2</sub>SnSe<sub>3</sub>, and a-Se. It is possible that extra selenium is present in CZTSe films because they are fabricated in a Se-rich condition. a-Se may also have a weak feature at ~235 cm<sup>-1</sup> due to the presence of crystalline-phase trigonal Se (t-Se) [23].

After the 2.47-mW illumination, the two main CZTSe peaks at 196 and  $172 \text{ cm}^{-1}$  exhibit both intensity reduction and redshift in three samples, as shown



Figure 7.7 Raman spectra of CZTSe and Si samples at 0.146 mW before and after being illuminated by high powers: (a) S1; (b) S2; (c) S3; (d) comparison of S1, S2, and S3; (e) comparison of different locations of S2; and (f) Si

in the spectra in Figure 7.7(a)–(c) (in green). In S1, the CZTSe main peak at  $195.3 \text{ cm}^{-1}$  shifts to  $193.0 \text{ cm}^{-1}$ , and  $172.1 \text{ cm}^{-1}$  shifts to  $171.7 \text{ cm}^{-1}$ . The redshift of the  $195-196 \text{ cm}^{-1}$  is the largest for S1 at 2.3 cm<sup>-1</sup>, compared with 1.3 cm<sup>-1</sup> for S2 and 0.5 cm<sup>-1</sup> for S3. These changes seem to suggest that the atomic bonds at the illuminated site are thermally expanded irreversibly as a result of the local heating if no atomic rearrangement occurs. However, it is possible that the redshift is

caused by the cation sublattice disordering, as suggested for CZTS [26], although the magnitude in CZTSe is much smaller (despite the higher excitation density in our case) and is sample-dependent. The exact mechanism remains to be examined by a direct structural probe (e.g., TEM), but it is likely not as simple as the proposed disordering effect. The weak features in the mesa-like band appear to smear out and weaken in both S1 and S2, as shown in Figure 7.7(a) and (b). In S2, a new feature at ~262 cm<sup>-1</sup> also emerges, whereas in S3 those weak features remain, but their relative intensities change—for instance, the peaks at ~235 and 250.5 cm<sup>-1</sup> become more apparent, as shown in Figure 7.7(c).

After illuminating further at 4.5 mW, with the spectra given in Figure 7.7(a)–(c) (in blue), the intensity of the strongest CZTSe peak initially at  $195-196 \text{ cm}^{-1}$ decreases further for all three samples. But the peak position remains nearly the same as that after the first HP illumination, except for S2; it shifts further from 194.8 to 193.5 cm<sup>-1</sup>, resulting in the largest redshift of 2.6 cm<sup>-1</sup> among all. For S1, as shown in Figure 7.7(a), the intensity of the 193  $\text{cm}^{-1}$  peak is reduced to only 25% of its original value before any HP illumination, and the  $172 \text{ cm}^{-1}$  mode becomes a weak shoulder from 168 to 178  $\rm cm^{-1}$ . Interestingly, for S2, the main CZTSe peak intensity decreases by a factor of 3, and the CZTSe peak of  $\sim 172 \text{ cm}^{-1}$  remains sharp. For the spectral region of the mesa-like band, a sharp peak emerges at 241.7  $\text{cm}^{-1}$  as the most prominent feature in S1 but not in S2 and S3. No significant further change occurs in S2 except that the feature of  $\sim 262 \text{ cm}^{-1}$  is slightly better resolved. In S3, the main peak intensity reduces only by about a factor of 2, but  $172 \text{ cm}^{-1}$  becomes nearly invisible. Also, a very strong sharp peak at 238.2 cm<sup>-1</sup> appears, which is accompanied by a second-order peak at  $478.2 \text{ cm}^{-1}$  (and a third-order peak at ~714 cm<sup>-1</sup>, data not shown) and a broad band at ~296 cm<sup>-1</sup>. Obviously, the second HP illumination brings more qualitatively different changes to these samples. The contrast between S1 and S2 suggests that the CZTSe structure prepared by coevaporation seems to be more robust than that prepared by sputtering against HPillumination-induced structural modifications.

Changes in Raman spectra from all three CZTSe samples after HP illumination indicate partial decomposition and plastic changes of the materials. However, different samples respond rather differently to HP illumination, indicating that seemingly similar CZTSe materials may differ significantly in their microscopic structures. The highest power applied to Si was, in general, safe for an epitaxial GaAs sample, but it could induce a structural change when a dislocation defect was illuminated [27]. Apparently, quaternary CZTSe is structurally not as robust as an elemental or binary semiconductor such as Si and GaAs. The contrast is mostly because of the difference in chemical bonding strength, but it may also because of the structural defects and lower thermal conductivity of the polycrystalline film.

2D Raman mapping is performed to examine the spatial extension of the local heating effect caused by HP illumination on the CZTSe samples, as shown in Figure 7.8 for 2.47-mW illumination. One random spot from each sample surface is first illuminated by 2.47 mW for 100 s. Raman mapping is then acquired with 0.146-mW laser power for a  $5 \times 5 \ \mu\text{m}^2$  or  $8 \times 8 \ \mu\text{m}^2$  area centered at the illuminated spot. For all the three samples, the illuminated spot appears darker after being illuminated, as shown in the optical images of Figure 7.8(a), (d), and (g). For each sample, Raman intensity mapping reveals a dark circle for the 196 cm<sup>-1</sup> peak, as shown in



Figure 7.8 S1, S2, and S3 Raman mapping after one spot being illuminated by 2.47 mW for 100 s: (a), (d), and (g) optical images of the illuminated spots (the red square indicates the area of Raman mapping); (b), (e), and (h) Raman mapping of the primary CZTSe mode at 196 cm<sup>-1</sup>; (c), (f), and (i) Raman mapping of the  $Cu_xSe_x$  mode at 261 cm<sup>-1</sup>

Figure 7.8(b), (e), and (h), which confirms the intensity reduction of this mode shown in Figure 7.7. In the Raman mapping of S1, a Raman peak at ~261 cm<sup>-1</sup> is observed in a ring outside of the illumination site (with ~4-µm diameter), as evident in Figure 7.8(c). However, in the mapping results of S2 and S3, the 261 cm $^{-1}$  peak is not observed, and the intensity maps of 220-270 cm<sup>-1</sup> show no significant spatial variation, as shown in Figure 7.8(f) and (i). The appearance of the 261  $\text{cm}^{-1}$  peak in S1 suggests the formation of  $Cu_x Se_v$  [28–31] occurring mostly at some distance from the illumination site, which likely results from a specific temperature profile caused by the laser heating. The formation of the ring structure also explains when measured at the illumination site, why the Cu<sub>x</sub>Se<sub>y</sub> feature is not resolved in S1 and S3, and is only very weak in S2, as shown in Figure 7.7(b). The Raman mapping of the primary CZTSe mode at 196 cm<sup>-1</sup> reveals most directly the spatial extension and that the material is being affected by the local heating. For S1, as shown in Figure 7.8(a), beyond the darkest 1- $\mu$ m circle (comparable with the laser spot size of ~0.76  $\mu$ m) at the illumination site, a dark area is observed with a diameter of  $\sim 3 \mu m$  comparable with the size of the 261 cm<sup>-1</sup> Cu<sub>x</sub>Se<sub>y</sub> ring. On the other hand, the illumination affects



0 x (μm)

0 2

x (µm)

2

4 μm

4 µm

(e)

y (µm)

-2

0

2

4

(h)

(d)

(g)

0.5

10.0 9.0

0.8 0.7 Intensity 0.0

5.0

4.0

3.0

(f)

y (µm)

(i)

Δ

0.5

2.5

2.0 .출

1.5 II

1.0

0.5

2

0 x (μm)

x (µm)

-2

-2 0 2

Figure 7.9 S1, S2, and S3 Raman mapping after one spot being illuminated by 4.5 mW for 36 s: (a), (d), and (g) optical images of the illuminated spots (the red square indicates the area of Raman mapping); (b), (e), and (h) Raman mapping of the primary CZTSe mode at 196 cm<sup>-1</sup>; (c) and (f) Raman mapping of  $Cu_x Se_y$  mode at 261 cm<sup>-1</sup>; and (i) Raman mapping of the t-Se mode at 238 cm<sup>-1</sup>

only an area of ~1.5  $\mu$ m diameter in S2 and less than 1  $\mu$ m diameter in S3. The difference between S1 and S2 seems to suggest that the two nominally similar films have rather different thermal conductivities, which might be partially responsible for the different responses in the structural change that we mentioned earlier. The extra layers above CZTSe in device S3 might improve the thermal conductivity of the structure as a whole; thus, it shows the least spatial extension. The contrast between S1 and S2 suggests that the CZTSe absorber layer prepared by the sputtering method (S1) is more sensitive to HP illumination than the film fabricated by the co-evaporation method (S2).

Figure 7.9 shows the mapping results with 0.146 mW after 4.5-mW illumination. Compared with the results of 2.47-mW illumination, larger affected regions are seen in the optical images in Figure 7.9(a), (d), and (g). Raman mapping in Figure 7.9(b) shows that the 196 cm<sup>-1</sup> peak intensity of S1 reduces in a circular region with a diameter larger than 6  $\mu$ m. The affected area of S2 in Figure 7.9(e) also enlarges to about 5  $\mu$ m in diameter. For S3, the affected area in Figure 7.9(h)

has a diameter only about 2  $\mu$ m. The extra layers in the CZTSe device again offer some protection to the CZTSe absorber. In the intensity map of the 261 cm<sup>-1</sup> peak, a Cu<sub>x</sub>Se<sub>y</sub>-rich ring still exists in S1 as shown in Figure 7.9(c), but now a similar Cu<sub>x</sub>Se<sub>y</sub> ring also appears in S2, although smaller, as shown in Figure 7.9(f). The size of the Cu<sub>x</sub>Se<sub>y</sub>-rich ring reflects the size of the heated region that reaches the optimal phase-transition temperature, which is comparable with the affected CZTSe area in S1 but smaller in S2. For S3, again, no Cu<sub>x</sub>Se<sub>y</sub> ring is observed. However, consistent with the observation of a strong Raman peak at ~238 cm<sup>-1</sup> shown in Figure 7.7(c) due to the formation of t-Se at the illuminated site under the same HP illumination the Raman map of 238 cm<sup>-1</sup> (Figure 7.9(i)) shows a bright region with a comparable size of the dark region for the CZTSe mode in Figure 7.9(h). The affected CZTSe area and the size of the Cu<sub>x</sub>Se<sub>y</sub> ring both depend on the thermal conductivity of the material, which differs significantly among the three samples.

It has been shown through TEM and other elemental studies that polycrystalline CZTSe films tend to exhibit various sizes of voids, domains of the secondary phases, and elemental segregation at the domain or interface boundaries, and these defects depend sensitively on the growth and postgrowth treatment conditions [32–34]. It is well known that grain boundaries and defects can have a major impact on the thermal conductivity, which in turn can significantly affect the size and shape of a new microstructures generated by local laser-heating-induced structural modification [35]. The structural modifications observed in the vicinity of the illuminated sites clearly indicate that S1 has a lower thermal conductivity than S2 and S3, implying that the film produced by sputtering is likely more defective. Furthermore, all these samples are likely to have a-Se as grown, and the sputtered sample has more inter-diffused Mo in the film, which is supported by the cleaved-edge Raman probe [36]. It is generally known that structural imperfections such as dislocations and grain boundaries reduce material thermal conductivity [37], but the substrate may also affect the thermal conductivity of a thin film [38]. In these CZTSe films, the Mo layer and glass substrate can, in principle, improve heat dissipation of the laser-induced heating, which yields a higher effective thermal conductivity. However, due to the low thermal conductivity of CZTSe [39] and short absorption length below the film thickness, the effect of the layers underneath is expected to be less significant. In fact, if it were significant, one would find the highest thermal conductivity in S1, which is apparently contrary to the experimental findings. Therefore, the lower crystallinity of S1 is likely the primary reason for its low thermal conductivity. In addition to revealing the microscopic-scale structural differences between samples, the HP illumination provides a way to generate new microscopic structures on an as-grown material for various possible applications, such as Cu<sub>x</sub>Se<sub>y</sub> rings in samples S1 and S2, and t-Se disks in sample S3. A similar method was used to generate graphene disks on an epitaxially deposited SiC [35].

### 7.5 Other applications

In Section 7.2, a CdS-rich region was found to yield lower EQEs and energy conversion efficiencies than the general area. However, these regions show much less



Figure 7.10 Reflectance and LBIC mapping with 532-nm laser at low and high power levels: (a) reflectance mapping at 532 nm; (b) histogram of (a); (c) LBIC mapping at 2  $\mu$ W; (d) histogram of (c); (e) LBIC mapping of 179  $\mu$ W; and (f) histogram of (e)

efficiency degradation at high illumination intensity, leading to an inversion of LBIC contrast in the area mapping as shown in Figure 7.10, which compares the LBIC mappings of the same area under two representative low and high laser powers. Here, "LP" means a level that can yield an average EQE comparable with

the macroscopic probe, whereas "HP" means the EQE of the general area that shows significant degradation, but the power is not as high as to cause permanent damage to the material. At the LP level, the device shows rather high average EQE for the 532-nm laser:  $67.9\% \pm 0.3\%$ , varying from 34.3% to 77.6%, which is consistent with the  $\sim$ 81% macroscopic EOE of a similar device. However, at the HP level, the average EQE reduces drastically down to  $17.7\% \pm 2.3\%$ . Interestingly, the reduction at the CdS-rich region is much smaller, from ~45% to ~25%, which leads to the reversal of the LBIC contrast, as evident from Figure 7.10(c) and (e). Clearly, the device region with a thicker CdS layer is more immune to the EOE droop with increasing illumination power, although the thicker region has a lower initial EQE. One possible mechanism could be that the electronic structure of the CZTSe/CdS heterojunction, such as the effective barrier height, depends sensitively on the CdS layer thickness. The low initial EQE of the CdS-rich region is likely related to the properties of CdS: the high reflectivity and residual absorption near the bandgap, and the poor carrier transport of the polycrystalline phase. These issues could, in principle, be mitigated or improved to allow the adoption of a thicker CdS layer-in particular, for high-illumination applications in either concentrated PV or photo-detection.

It is well-recognized that elementary ratios of Cu, Zn, Sn, and S(Se) within the CZTS(Se) absorber layer can greatly impact the CZTS(Se) solar cell performance. Empirically, the Cu-poor and Zn-rich condition tends to offer better performance than stoichiometry when the stoichiometry condition prompts point-defect formation [9,11,40,41]. However, it is also reported that the cell with elemental ratios closer to stoichiometry is more immune to EQE droop than that more off-stoichiometry. The variation in elemental ratios results not only in fewer or more defects but also in changes to the band alignment at the absorber/back-contact interface, absorber/window-layer interface, or both [42].

Figure 7.11 shows LBIC mappings obtained from the same area of a CZTSe solar cell (S4) at LP and HP illumination. The average EOE of S4 at LP level is 58.4% from Figure 7.11(a). However, at HP level, as shown in Figure 7.11(b), the average EQE of S4 is 55.5%. Comparing the histograms in Figure 7.11(c) and (d), the result at HP is similar to that at LP, i.e., there is almost no EQE droop. Raman spectra obtained from S4 and the CZTSe cell measured in Figure 7.2 show very similar CZTSe and CdS Raman modes and intensities, as shown in Figure 7.12. In other words, it is not the variation in CdS layer thickness that leads to the different EQE droops. The main difference between the two cells is the Cu/(Zn+Sn) and Zn/ Sn ratios in the absorber. Therefore, the difference in the elemental ratios is likely to be the main cause of the different illumination density dependencies. CdS/ CZTSe is mostly found to have a "spike"-like alignment, in which the conduction band minimum (CBM) of CdS is higher than that of CZTSe. Type I alignment benefits in  $V_{\rm OC}$  but becomes a barrier for carriers moving across the heterojunction. Increasing the Zn/Sn ratio is expected to increase the CBM of CZTSe, which is beneficial for electron collection. Thus, CZTSe devices with higher Zn/Sn and lower Cu/(Zn+Sn) ratios usually yield better photo-response. However, when illuminated with HP density, raising of the electron Fermi level might lower the



Figure 7.11 S4 LBIC mapping with 532-nm laser at low and high power levels: (a) at ~2  $\mu W$ ; (b) at ~179  $\mu W$ ; (c) histogram of (a); and (d) histogram of (b)



Figure 7.12 Raman spectra of S2 and S4 from a random spot

electron barrier at the back contact, which might allow electrons to leak out through the back contact. Thus, materials with higher Cu and lower Zn content or their ratio closer to stoichiometry, which are expected to have a higher Mo back electron-

blocking barrier, could still generate a relatively high EQE at HP illumination, despite that the initial short-circuit current is lower at low illumination density because of unfavorable band alignment between CZTSe and CdS. In addition, an CZTSe absorber with closer-to-stoichiometry elemental ratios might be less defective, which could be beneficial to the device performance. As demonstrated in a recent comparative study of inorganic and organic–inorganic hybrid PV materials, specifically, GaAs and CdTe vs. CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, the most important reason for the impressive performance of the hybrid perovskite is that it tends to have much less detrimental point defects than its inorganic counterparts [43]. The structural defects lead to lower PL efficiencies in the inorganic materials at the low illumination density (e.g., close to 1 Sun). The defects could very well be the reason for the low open circuit voltage in the CZT(S,Se) cells, which is one of the key challenges to improve their efficiencies. To conclude, there might be alternative approaches to optimize the device performance other than altering the stoichiometry, which also depends on the device operation condition.

## 7.6 Summary

Integration and correlation of multiple nondestructive spatially resolved techniques is a powerful characterization approach to study the optoelectronic properties of thin-film solar cell materials and devices, as demonstrated for CZT(S,Se) in this chapter. µ-Raman spectroscopy, revealing the "fingerprints" of the material structures and compositions, was used to analyze the chemistry in CZT(S,Se) films. µ-PL was used to estimate the bandgap of CZT(S,Se) and detect possible defects within the film.  $\mu$ -LBIC was used to probe the photo-response of CZT(S,Se) solar cells in different illumination densities and to visualize the structural defects and the impact of microscale film inhomogeneity at the same time.  $\mu$ -Reflectance offers a more accurate method to estimate the reflectance loss of a rough sample surface—especially to compare the general CZT(S,Se) area with nonuniform regions. SEM and AFM were used to characterize the surface morphology. By applying this approach, in conjunction with high-temperature and high-excitation-power optical spectroscopy, one can probe the microscopic-scale variations between samples and devices that appear to be very similar from macroscopic material and device characterizations. Thus, the approach serves as a very useful tool to understand the underlying microscopic material structures, provides hints for future improvement in material quality and device design, and predicts the potential of improvement in device performance.

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