



Nanoscale Measurements of the Surface Photovoltage in $\text{Cu}(\text{In,Ga})\text{Se}_2$, Cu_2ZnSn_4 , and $\text{Cu}_2\text{ZnSnSe}_4$ Thin Films: The Role of the Surface Electronics on the Efficiency of Solar Cells

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NANOSCALE MEASUREMENTS OF THE SURFACE PHOTOVOLTAGE IN $\text{Cu}(\text{In,Ga})\text{Se}_2$, $\text{Cu}_2\text{ZnSnS}_4$, AND $\text{Cu}_2\text{ZnSnSe}_4$ THIN FILMS: THE ROLE OF THE SURFACE ELECTRONICS ON THE EFFICIENCY OF SOLAR CELLS

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ABSTRACT

We report on recent advances in the development of nanoscale measurements of the surface photovoltage (SPV) based on scanning tunneling microscopy (STM) and its application to the kesterites $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe). One critical aspect of the electronic structure of $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) that has yet to be determined in their related kesterite compounds is the character of the surface electronics. In CIGS, spontaneous deviations in the stoichiometry of the surface cause a depletion (or even a type inversion) region that reinforces the CIGS homojunction. First-principle calculations predict that this inversion region will be more difficult to form in CZTS. In this contribution, the characteristics of the surface space charge region for both CIGS and CZTS(e) are investigated by STM. The implications of the results of these measurements on the future development of CZTS solar cells will be discussed.

INTRODUCTION

$\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) has recently demonstrated a record efficiency of 20.3%, the absolute record for all thin-film photovoltaics (PV) [1]. The success of CIGS is based primarily on its electronic structure which, in the regime of Cu deficiency, is dominated by the formation of Cu vacancies and the stabilization of defect complexes with low formation energies [2,3]. First-principle calculations predict that our understanding of the electronic structure and defect formation in CIGS can be partly extrapolated to the kesterites $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) [4,5].

One critical aspect of the electronic structure of CIGS that has yet to be determined in CZTS (for both sulfides and selenides) is the character of the surface electronics. In CIGS, spontaneous deviations in the stoichiometry of the surface cause a depletion (or even a type inversion) region that reinforces the CIGS homojunction [6]. First-principle calculations predict that this inversion region will be more difficult to form in CZTS [5]. This may be one negative factor limiting the future development of CZTS solar cells that needs to be addressed.

In this contribution, the characteristics of the surface space charge region for both CIGS and CZTS and CZTSe are investigated by scanning tunneling microscopy (STM). The surface photovoltage (SPV) is determined by measurements of the contribution of the local photocurrent to the tunneling current while sweeping the voltage applied to the conductive tip. Another benefit of the STM is that

nanoscale fluctuations of the SPV and multiple phases with different surface electronics can be resolved.

EXPERIMENTAL

Figure 1 shows the schematics of the STM equipped with the optics for the SPV measurements. A modulated optical beam (at a frequency above the response time for the z-feedback control of the STM of $f > 2$ kHz) is used to generate an excess of minority electrons in the p-type semiconductor. The contribution of the transient photocurrent (I_{ph}) to the tunneling current (I_t) is obtained by lock-in detection at the modulation frequency. The optical chopper easily runs at frequencies above the tens of kHz, avoiding thermal expansion of the vacuum gap and allowing optimum settings (integral and proportional gains) for imaging in constant current mode with the STM.

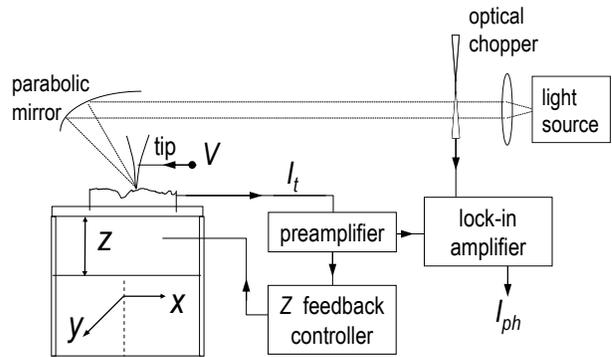


Figure 1 Schematics of the setup used in the STM measurements of the SPV.

CZTS thin films are obtained by coevaporation of Cu, Zn, and Sn from three independent effusion cells under a molecular beam of S_2 supplied by a valved-cracking source. The molybdenum-coated glass substrates are actively heated to 470°C . The base pressure of the chamber is 8.0×10^{-6} Torr, rising to 1.7×10^{-4} Torr during the deposition. More details, including information on the elemental sources, can be found in [7]. The stoichiometry of the films used in this study is confined to the region of stability for the CZTS kesterite and is slightly displaced towards the ZnS-SnS_2 boundary of the phase diagram. These CZTS films are therefore Cu-poor ($\text{Cu}/(\text{Zn}+\text{Sn}) \sim 0.74$) and Zn-rich ($\text{Zn}/\text{Sn} \sim 1.36$), which is consistent with the stoichiometry of the best CZTS solar cells reported in the literature [8,9].

CZTSe thin films are obtained by a two-stage coevaporation process as described in Ref. 10. The molybdenum-coated glass substrates are actively heated to 470°C to 500°C. Under an overpressure of Se and Sn, Cu is delivered at a high rate during the first stage to form Cu-rich CZTSe, and then Zn continues to be delivered in the second stage to adjust the Cu/Zn ratio and form Cu-poor CZTSe. Similarly to the sulfides, the selenide films used in this study are Cu-poor ($\text{Cu}/(\text{Zn}+\text{Sn}) \sim 0.9$) and Zn-rich ($\text{Zn}/\text{Sn} \sim 1.1$).

Finally, CIGS thin films are obtained by the three-stage coevaporation process. The $\text{Cu}/(\text{In}+\text{Ga})$ ratio for our reference CIGS is ~ 0.9 and the $\text{In}/(\text{In}+\text{Ga}) \sim 0.3$, as required for record performance [11].

All of these thin films are stored in inert (nitrogen) atmosphere before being loaded in the vacuum chamber of the STM. The native oxide must be present as no surface treatments are applied prior or during the measurements.

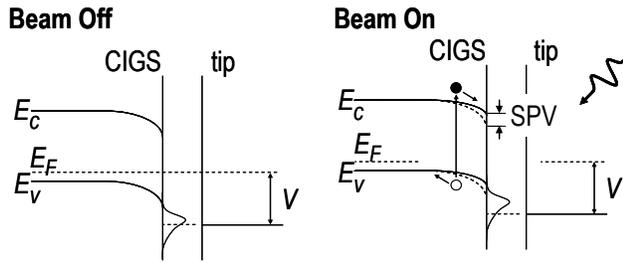


Figure 2 Generation of a photovoltage at the surface of CIGS.

RESULTS AND DISCUSSION

The origin of the surface photovoltage is illustrated in Figure 2 [12,13] for CIGS. In the absence of illumination, we assume a depletion region ($\Delta p <$) near the CIGS surface, which causes a downward band bending [5]. Photoexcited minority electrons diffuse and accumulate at the surface, hence reducing the band bending. Photoexcited majority holes diffuse in the opposite direction. As a result, a transient in the tunneling current is observed and measured as I_{ph} using the lock-in detection under the modulated optical beam. With the beam on, the semiconductor surface is driven away from equilibrium, and the surface potential shifts; a SPV arises. The modulation frequency of the optical chopper is fast enough that the steady state is not achieved during the cycle. The magnitude of the SPV depends on the energy of the pinning of the Fermi level, the width of the surface space charge region, and the recombination. Therefore, multiple properties from both the surface and subsurface of the film contribute to the SPV. For a more detailed description, including pinning of the Fermi level and surface states, see Ref. 13. In our case, SPV measurements can detect the presence of a homojunction in the CIGS or CZTS film before the solar cell is fully processed (CdS and ZnO depositions).

Figure 3(a) shows a constant current mode STM image of a CIGS thin film, acquired at $V = -1$ V and $I_t = 500$ pA. For CIGS, the STM operation is stable when applying a negative voltage to the tip (electrons tunneling from the tip) and becomes unstable when applying a positive voltage (holes tunneling from the tip). This is consistent with a surface depletion region ($\Delta p <$) when considering the rectifying characteristics of the tunneling junction. The existence of such a depletion region is confirmed by measuring the contribution of the transient photocurrent (I_{ph}) to the tunneling current (I_t) while sweeping the tip voltage [see Fig. 3(c)]. The maximum photocurrent is measured at $V \sim +2$ V and, consequently, the intrinsic level is well below the Fermi level ($E_i < E_f$), causing an inversion at the surface (from p -type to n -type). The formation of this homojunction is critical to improving the efficiency of CIGS solar cells.

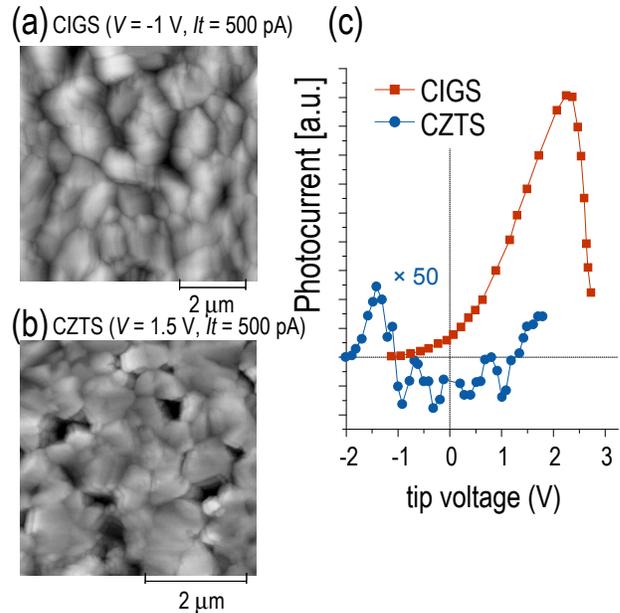


Figure 3 (a) STM image of a CIGS film. (b) STM image of a CZTS film. (c) Photocurrent measured in CIGS and CZTS as a function of the voltage applied to the tip.

Because of the similar electronic structure of chalcopyrites and kesterites, we can anticipate that CZTS will benefit from a surface electronics comparable to that of CIGS. Figure 3(b) corresponds to a STM image of a $\text{Cu}_2\text{ZnSnS}_4$ thin film, acquired at $V = +1.5$ V and $I_t = 500$ pA. Interestingly, the STM reproduces the microstructure of the CZTS at positive voltage, which is opposite to our observations for CIGS. Figure 3(c) shows the effect of the tip voltage on I_{ph} for the kesterite film. The interpretation of these results is more difficult than in CIGS. The magnitude of the SPV is much reduced in the CZTS film, and the photocurrent seems to be dominated by surface electronic states. At low tip voltage (for both polarities), we observe a current of holes diffusing towards the surface associated with distinct surface states within the band gap. The

polarity of the photocurrent reverses at higher values of the tip voltage (near and above the band gap), although the level of the photocurrent is at least one order of magnitude below that of CIGS. These results suggest that (i) either the depletion region is very weak in the CZTS film or (ii) the recombination within the space charge region is very high and its contribution to the SPV signal is largely reduced.

The absence of an inversion region near the surface of the kesterite structure can be a direct consequence of the much higher energetic preference for acceptor states in kesterites relative to chalcopyrites, leading to n-type doping difficulty [5]. The “doping pinning rule” proposed by Zhang et al. [14] can be applied to determining the dopability of these compounds. Thus, the energy of the Fermi-level pinning for n-type doping is above the conduction band minimum (CBM) of CuInSe_2 and below the CBM of CZTS, as shown in the band diagram of Figure 4 [5,15]. Consequently, the n-type doping is more difficult in CZTS than it is in CuInSe_2 . That said, the higher recombination in the kesterites associated with substitutional defects leading to transition energy levels close to the midgap (Cu_{Sn} , Sn_{Cu} , and Sn_{Zn}) can overrun the potential beneficial effects of such a depletion region.

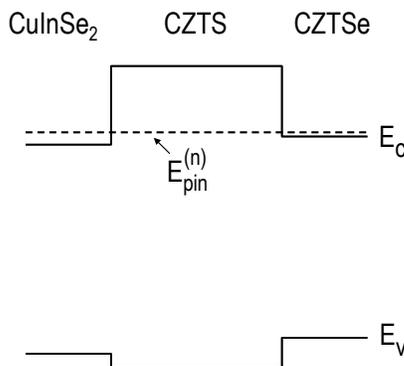


Figure 4 Band alignment and pinning energy of the Fermi level for n-type doping in CuInSe_2 , CZTS, and CZTSe.

The prospect of finding the inverted surface in the selenides is much higher than in sulfides because of the band alignment between CuInSe_2 , CZTS, and CZTSe (see Fig. 4). The lower band gap of the selenide allows for the pinning energy of the Fermi level to move towards the CBM of CZTSe, improving the n-type dopability of the selenide.

Similar STM measurements of the SPV are then performed to probe the surface electronics of the selenide. Fig. 5(a) corresponds to a STM image of a $\text{Cu}_2\text{ZnSnSe}_4$ thin film acquired at $V = +1.5$ V and $I_t = 500$ pA. As is the case for the sulfide, the STM reproduces the microstructure of the selenide only at positive voltage. Figure 5(b) shows the effect of the tip voltage on I_{ph} for the

CZTSe film. A transient photocurrent is measured when applying a negative bias to the tip. No response is observed when reversing the polarity of the tip.

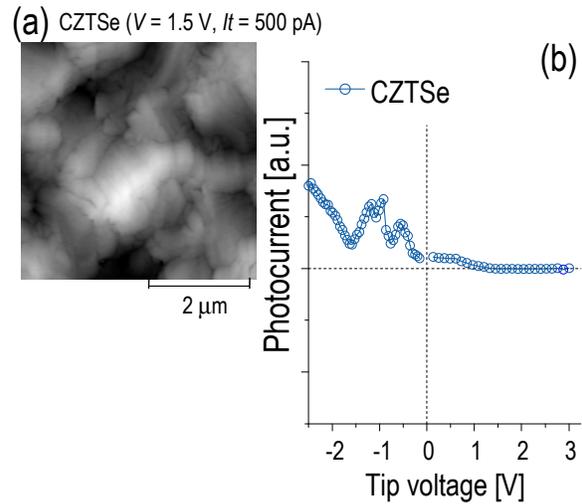


Figure 5 (a) STM image of a CZTSe film. (b) Photocurrent measured in CZTSe as a function of the voltage applied to the tip.

In CZTS, the photocurrent I_{ph} saturates rapidly when increasing the intensity of the external illumination, suggesting that a limited number of states is involved in the effect (i.e., surface electronic states). In CZTSe, on the other hand, the photocurrent increases linearly with the excitation, suggesting surface band bending, as is the case for CIGS. However, this band bending is of opposite sign to that seen in CIGS, which is consistent with a surface *accumulation* region ($\Delta p >$) when considering the rectifying characteristics of the tunneling junction. Unfortunately, an accumulation region (upward band bending) near the surface will work against the collection of the photocurrent in the solar cell. On the other hand, the band bending that leads to accumulation in CZTSe is not as pronounced and the impact over the cell characteristics is limited. As is the case for CZTS, the presence of a depletion region can be difficult to detect if the recombination in the film is high enough. The observed behavior can be simply explained by charged states in the native oxide.

These results show that, at this stage of development, the surface photo response from the kesterites is very different from their related chalcopyrites, and the beneficial effects of the surface depletion observed for the chalcopyrites do not arise spontaneously in kesterites. If the presence of such a depletion region proves to be critical to the efficiency of CZTS(e) solar cells, we suggest to investigate different variations of the surface stoichiometry during the growth and/or the introduction of impurities that improve the n-type dopability of kesterites.

SUMMARY

In summary, we have investigated the surface photovoltage of chalcopyrites and kesterites (both selenides and sulfides) by STM-based measurements. The photo response from the surface of the chalcopyrites is much more pronounced than from kesterites, most likely because of the high recombination in the CZTS(e) films. The main contribution to the SPV in the kesterites is then associated with surface/interfacial electronic states. These results are based on kesterite films in the early stages of development and, therefore, we can anticipate changes in the surface electronics as the quality of the films improves. What is certain is that advancing our understanding of the effects of stoichiometry, surface reconstruction, and dopability will be needed to improve the characteristics of the junction and the performance of kesterite solar cells.

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