Investigation of micro-electrical properties of $\text{Cu}_2\text{ZnSnSe}_4$ thin films using scanning probe microscopy

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Abstract

We report on a local potential and resistance mapping of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) films using nm-resolution electrical scanning probe microscopies of scanning Kelvin probe force microscopy and scanning spreading resistance microscopy. We have conducted a comparative study with high-performance $\text{Cu}_2(\text{In,Ga})\text{Se}_2$ (CIGSe) film. Both CZTSe and CIGSe were deposited by co-evaporation of elements in vacuum. The results show that the microelectrical properties of the two polycrystalline materials are similar—higher potential and lower resistance on the grain boundaries (GBs) than on grain surfaces—suggesting inverted GB carrier polarity of these films. The consistent GB properties in contrast to the large difference in photovoltaic output of the two materials suggest that factors other than the GBs are responsible for the low photovoltaic output of CZTSe device.

Key Words: CZTSe; solar cell, thin film; grain boundary; scanning Kelvin probe force microscopy; scanning spreading resistance microscopy.

1. Introduction

Earth-abundant $\text{Cu}_2\text{ZnSnS}_4(\text{Se})$ [CZTS(Se)] solar cells have been greatly improved to efficiency of $E_{\text{ff}}=12.6\%$ and attracted great interests [1]. The crystal structure of this kesterite resembles to chalcopyrite $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGSe), with the group III elements being replaced by Zn in one cation plane and by Sn in the next cation plane. It is believed that the two photovoltaic (PV) materials should share many similarities [2]. However, efficiencies of the current record solar cells made of the two thin film absorbers and the same other device components (buffer, window, and back contact) are much different, being $>20\%$ [3] and 12.6% , respectively. Short carrier lifetime ($\tau \sim 1\text{-}10$ ns) [4-6] of CZTS is clearly one of the main reasons, possibly due to the intense point defects in the grain bulk of the polycrystalline thin film. This order of lifetime would cause a diffusion length of $\lambda \sim 0.5$ μm [6], which is compatible with the grain size of the film. Therefore, grain boundaries (GBs) can be another factor negatively affecting the device efficiency if the GBs are active for minority carrier recombination.

High performance CIGSe, on the other hand, reached a lifetime of $\tau \sim 100$ ns [7]. Major point defects in this material form self-compensated complex of $(2\text{V}_{\text{Cu}} + \text{In}_{\text{Cu}}^{2+})$, which is benign for minority carrier recombination [8,9]. With this degree of high quality grain bulk, GBs can be a bottle-neck limiting factor for solar cell efficiency if the GBs are active for recombination. However, many theoretical modeling [10,11] and microscopic studies [12-15] have pointed to a self-compensated GB with electrically benign for the recombination.

Scanning probe microscopy (SPM)-based characterizations are one of the major studies for the electrical properties of individual GBs [12-14]. Combining the results [12,13] based on two

SPMs of scanning Kelvin probe force microscopy (SKPFM) [16] and scanning spreading resistance microscopy (SSRM) [17], we have proposed an inverted GB polarity of CIGSe, i.e., the doping or carriers in the space charge region around the GBs is n-type, inverted from its p-type grain bulk [13]. The potential mapping by SKPFM showed that the CIGSe GBs are positively-charged, or in other words, the GBs are either depleted or inverted [12]. The lower resistance along the GBs than in the grain bulk, then, indicates an inverted GB for this thin film material [13]. In this paper, we study on the CZTSe polycrystalline thin film, in a similar approach. Despite the large PV output difference of the two materials [18,19], we found that the potential and conductance of the two materials share many similarities, indicating that the current low PV output of CZTSe is caused by defective grain bulk and grain surfaces, such as secondary phases, stoichiometry, and structural defects etc., rather than negative contribution from GBs.

2. Experimental

The CZTSe films were deposited by physical vapor deposition in vacuum from four element sources of Cu, Zn, Sn, and Se, on Mo-coated solder-lime glass substrate. Prior to the film deposition, a 15nm NaF was evaporated for providing adequate Na in the film growth, which is crucial for the high-performance film. The experimental procedure and control parameters used for depositing the films yielded NREL's current best CZTSe device with a conversion efficiency of $E_{ff}=9.8\%$ [20].

Both SKPFM and SSRM are based on an atomic force microscopy (AFM) of Veeco D5000 and Nanoscope V controller. The AFM is set in an Ar glove box with both H_2O and O_2 concentrations less than 0.1 ppm to protect the film from oxidation, because a large indentation force (>1000 nN) and a relatively high bias voltage (~ 3 V) are applied between the probe and film in the SSRM measurement. SKPFM uses the mode of second harmonic frequency (300-400k Hz) [21] and a PtIr-coated Si tip (Nanosenser, PPP-EFM). The energy and spatial resolutions are ~ 10 mV and ~ 30 nm, respectively. The Kelvin probe voltage and the ac voltage are applied to the tip and the sample is grounded. In this setup, the Kelvin probe signal represents the electrostatic potential of the sample; a higher potential in a potential image indicates a positively-charged local area with a smaller local workfunction. In the SSRM measurement, a highly doped diamond-coated Si tip (Bruker-nano, DDESP) with a nominal radius of ~ 35 nm was employed because of its strong resistance against wearing off. The bias voltage was applied to the sample and the tip was virtually grounded. "Dark Lift" mode, which scans the second time with the line profile obtained from the first scan and with the AFM laser being turned off, was used to verify whether the resistance measurement is affected by the AFM laser. All the results shown in this paper are not affected by the AFM laser because the probe cantilever blocked most of the laser beam, or in other words, the laser illumination is sufficiently small compared with the film carrier concentration [13]. Therefore, all the results are dark properties of the PV materials.

3. Results and discussion

Fig. 1 shows a SKPFM potential, the corresponding SSRM resistance, and the corresponding AFM images, taken on the same area of the CZTSe film. Scale bars are linear in the SKPFM and AFM images, and logarithm in the SSRM image. The middle value in the scale bar of the resistance image is an average over the image. With a positive sample bias voltage ($V_s > 0$), a brighter area in a resistance image represents a larger resistance value, and when the bias is negative ($V_s < 0$), a bright area represents a smaller resistance value. To display the contrast best, the ranges of the scale bars are set much larger than the real data ranges of the images. Fig. 1(d)

and (e) show example line profiles along the lines in the potential and resistance images. The changes in the potential and resistance are about 200 mV and within one order of magnitude, respectively.

From the potential image, one sees that the potential on the GB is higher than on the grain surface, indicating positively-charged GBs. This positive charge makes a downward band bending in the space charge region around the GB. However, because surface charges also make a band bending in the surface space charge region, which tends to reduce the potential contrast between the GB and grain surface, we cannot determine the amount of band bending around the GB in the film bulk [12]. Therefore, the GBs should be either depleted or inverted in the film bulk. This scenario of potential distribution is similar to the high performance CIGS film, which exhibited higher potential on all the GBs except for the coherent $\Sigma 3(112)$ GB [12].

As indicated on the scale bar, the average resistance over the resistance image is $R=6.6 \times 10^5 \Omega$. This absolute value of resistance corresponds to an average resistivity of $\rho=9.2 \Omega\text{cm}$, using $R=\rho/4r$ where $r=35 \text{ nm}$ is the effective radius of the probe/sample contact, and further to a carrier concentration $C=7 \times 10^{16}/\text{cm}^3$ using a mobility of $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [22-25]. This value of carrier concentration is roughly consistent with the capacitance-voltage (C-V) measurement of our CZTSe film [5]. There two parameters of the effective contact radius and mobility when converting the measured resistance to carrier concentration. The first one, effective contact radius, can be overestimated by the use of nominal probe size (radius of the round shape of probe apex) [13,26], because not every local area at the probe/film interface can open adequate conductance channels, depending on the local bonding configurations. The mobility value in the literature is in a range of $3\text{-}30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [22-25]. Therefore, this measurement of carrier concentration using SSRM is semi-quantitative, and we believe in the rough order of magnitude but not in the accurate number. In fact, SSRM is a technique for imaging the local resistivity in qualitative scale with nm fine spatial resolution, rather than a technique measuring the quantitatively-absolute resistivity value.

The inhomogeneity of resistance is within one order of magnitude, reflecting the doping inhomogeneity of the polycrystalline thin film. This nonuniformity is among the grains and inside grains. From the resistance map of Fig. 1(b), one sees a low resistance or high conductance channel along the GBs of the film. The low resistance is observed in most of the GBs. However, there is a low percentage of the GBs with higher resistance, for example, GBs ‘A’ and ‘B’ in Fig. 1(b). This discrepancy of low and high resistance on the GBs is different from the potential image of Fig. 1(a), where all the GB potentials were measured higher than the grain surface. It is also different from the high performance CIGSe films where all the GBs showing higher potential exhibited lower resistance [13]. As discussing later, this higher GB resistance is likely caused by insufficient spatial resolution of SSRM when imaging some of the GBs with narrow regions of inverted carrier polarities.

The width of the GB low resistance region is in 30-120 nm (Fig. 2), with 40-50 nm being the most populated. This channel width is smaller than CIGS where the range is 30-150 nm and with 50-70 nm being the most populated. Similar to the CIGSe film, we attribute this lower GB resistance to inverted carrier polarity around the GBs [13]. The higher GB potential indicates that the GB is either depleted or inverted. This lower resistance proposes an inverted GB but not a depleted GB. If the GB is depleted, the resistance in the space charge region around the GB would be larger than the grain interior, which is opposite to the measurement. This lower resistance should not be through the “pure” GB where defective atomic arrangement with only a few atomic layers likely scatters the carrier transport. Therefore, we simulated the carrier concentration around the GB (Fig. 3) using PC1D software [27], and using 1 nm GB width with an n-type doping of

$5 \times 10^{19}/\text{cm}^3$ and a grain bulk p-doping of $5 \times 10^{16}/\text{cm}^3$. The width of inversion region, where the electron concentration is higher than hole, is 95 nm. The width with the electron concentration higher than the bulk p-doping ($5 \times 10^{16}/\text{cm}^3$) is 15 nm. Considering that the electron mobility can be one order of magnitude higher than hole, the width of the low resistance channel with electron concentration higher than $5 \times 10^{15}/\text{cm}^3$ is 25 nm. Therefore, the low resistance channel width should be between 15 nm and 25 nm. This width depends mainly on the bulk p-doping concentration, and is significantly smaller than that of CIGS (35-65 nm) with a smaller p-doping concentration ($1 \times 10^{16}/\text{cm}^3$) [13]. Indeed, C-V measurement showed a significant higher carrier concentration of CZTSe than CIGSe [5], and our SSRM measurement also shows a smaller overall resistance of CZTSe ($R=6 \times 10^5 \Omega$) than CIGS ($R=9 \times 10^6 \Omega$). The consistency of the narrower low resistance width of CZTSe with the higher bulk doping concentration than those of CIGSe supports the argument that the low resistance channel on the GBs originates from the inversion of GB polarity.

The width of low resistance channel from the measurement (40-50 nm) is significantly larger than the simulation results (15-25 nm), which could be a result of insufficient spatial resolution with the diamond-coated probe (nominal diameter 70 nm). The spatial resolution on Si micro-devices was claimed to be sub-10 nm [28]. In this measurement, a critical condition for the improvement of resolution is the setup in a high-vacuum (10^{-5} Torr), which is comparable with our setup of an Ar glove box in terms of O_2 and H_2O concentrations. However, the SSRM technique, including spatial resolution and resistance sensitivity, should depend closely on the sample materials because the probe/sample contact is critical in the measurement and it is highly material-dependent [13,26,29]. Therefore, we believe that the spatial resolution in our measurement is ~ 30 nm, as inferred from the smallest low resistance width, which is larger than the simulation result. Although SSRM measures the spreading resistance across the film and thus involving a large volume of the sample, the voltage drop concentrates mainly on a small volume of the material right beneath the probe/film interface, leading to the superior spatial resolution for imaging the nm-scale contrast of the local resistivity [28,29]. As shown above, the low resistance was observed on most of the GBs, and high resistances were observed in a low percentage of the GBs. The higher resistance is likely due to the insufficient spatial resolution of the SSRM technique if the inversion region around the GBs is further narrow so that SSRM can no longer resolve the GBs. However, we cannot exclude the possibility that the GB resistance is higher than the grain bulk. In this case, the GB should be depleted but not inverted. A depleted GB is generally considered to have charged deep levels in the bandgap and to be active for minority carrier recombination.

SSRM measures the overall resistance from the probe to the back contact of the sample, which includes the probe/sample contact resistance, the spreading resistance through the sample, and the resistance of back contact. The back contact resistance involved in the measurement is small, considering that the solar cell series resistance is at most $1\text{-}2 \Omega\text{cm}^2$ and that the current route is spread out when reaching the back contact. Therefore, minimizing the probe/sample contact resistance is critical in the SSRM measurement [13,17,26,28,29]. On Si micro-devices, it was minimized by indenting the probe into the material, making local high-pressure phase of β -tin and BCT5-Si [29]. These high-pressure phases have nonlocalized molecular orbitals of sp^3d^1 and sp^3d^2 with metallic-like behavior. Similar to Si, we have minimized the contact resistance on CIGS by indenting the probe and applying a bias voltage V_s larger than the onset voltage of the probe/sample barrier [13]. For the CZTSe film, we minimized the contact resistance using similar approach. The overall resistance drops sharply with increasing the contact force [Fig. 4(a)] and gets saturated with a force $F > \sim 1000$ nN. The contact under the large indenting force shows a moderate rectifying current-voltage (I-V) characteristic [Fig. 4(b)], but not an ideal Ohmic contact,

indicating that the contact has a barrier with serious current leaking. Because the measured resistance ($R=6\times 10^5 \Omega$) was converted to a reasonable carrier concentration of $C=7\times 10^{16}/\text{cm}^3$ [5] with a reasonable mobility value of $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [22-25], the contact resistance should be minimized to a low level, which does not dominate the imaged resistance contrast.

With a small contact force or a reverse V_s polarity, the resistance mapping shows different images from Fig. 1(c); this should be dominated by the contact resistance [13,26]. Fig. 5 shows a resistance and the corresponding AFM images with a small indentation force of $F=50 \text{ nN}$ and an adequately-large voltage of $V_s=2 \text{ V}$. In this condition, the overall resistance ($3.0\times 10^7 \Omega$) is much larger than $F>1000 \text{ nN}$ and the resistance on the GBs is not well defined, unlike the case of Fig. 1(c). The resistance map is likely dominated by grain facet features of the film surface, possibly related to the facet-oriented contact barrier. With changing V_s , the resistance images under a large indenting force are similar when V_s keeps the forward polarity [Fig. 6(a)-6(c)], all showing the low resistance channel along the GBs. As indicated by the I-V curve of Fig. 4(b), significant current flows with $V_s>+0.5 \text{ V}$. The contact resistance in this bias voltage should be sufficiently minimized and the overall resistance should be dominated by the local spreading resistance beneath the probe. With the reverse V_s , the overall resistance [Fig. 6(d)—6(f)] is significantly larger than under the forward V_s . In this case, the resistance is larger on the GBs than on the grain surface, opposite to the case under a forward V_s . Considering the significant leaking current under a reverse V_s , this resistance contrast could be a result of nonuniform leaking barrier with the contact on grain surface being more leakage than on the GBs.

The micro-electrical properties of the CZTSe films are similar to our three-stage high-performance CIGSe films—the potential on the GB is higher than on grain surface and the resistance is lower [12,13]. Therefore, like the CIGSe film [13], we propose an inverted GB polarity of the CZTSe film. This inverted GB should have no deep levels and should not be recombination center for minority carriers, because if there mid-gap states, the Fermi level should be pinned at the states and the space charge region around the GB should be depleted but not inverted. Despite this similarity of the two polycrystalline films, the PV outputs of the devices with all similar other device components (CdS buffer and ZnO transparent conductive oxides layers) are in a large gap [1,3,18,19]. This PV output difference should be dominated by factors other than the GBs, such as secondary phases, deviation of stoichiometry from the optimal, and structural defects on the grain surface and in the grain surface etc. In fact, photoluminescence measurement showed much shorter minority carrier lifetime of CZTSe than CIGSe [4-7]. Other micro-optoelectrical characterizations also show consistent results that the GB properties of CZTSe film are similar to that of CIGSe [30].

4. Summary

The micro-electrical properties of CZTSe thin films were investigated by using SKPFM and SSRM, and compared with our high-performance CIGSe films. The potential mapping shows a higher GB potential than on the grain surface, indicating a positively charged GB, or in other words, the GBs are either depleted or inverted. The resistance mapping shows a lower resistance channel along most of the GBs, suggesting an inverted GB polarity but not a depleted GB. In the SSRM measurement, an indentation force larger than 1000 nN and a forward V_s larger than 0.5 V are necessary for minimizing the probe/film contact resistance so that the spreading resistance beneath the probe can be measured. All these characterization results are similar to the high performance CIGSe films, suggesting that the present large PV performance gap between the two materials is caused by factors other than the GBs.

Acknowledgement

The authors thank C. DeHart and J. Carapella at NREL for the assistances in making solar cells samples. This work was supported by the U.S. Department of Energy under Contract No. DOE-AC36-08GO28308 with the National Renewable Energy Laboratory.

References

- [1] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, and D.B. Mitzi, Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency, *Adv. Energy Mater.* 2013, DOI: 10.1002/aenm.201301465.
- [2] S. Chen, A. Walsh, X.-G. Gong, and S.-H. Wei, Classification of lattice defects in the kesterite $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ earth-abundant solar absorbers, *Adv. Mater.* 25 (2013) 1522-1539.
- [3] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, and E.D. Dunlop, Solar cell efficiency table (version 42), *Prog. Photovolt: Res. Appl.* 21 (2013) 827-837.
- [4] S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, K.T. Todorov, and D.B. Mitzi, Low band gap liquid-processed CZTSe solar cell with 10.2% efficiency, *Energy and Environmental Science* 5 (2012) 7060-7065.
- [5] I.L. Repins, M.J. Romero, J.V. Li, S.-H. Wei, D. Kuciauskas, C.-S. Jiang, C. Beall, C. DeHart, J. Mann, W.-C. Hsu, G. Teeter, A. Goodrich, and R. Noufi, Kesterite successes, ongoing work, and challenges: a perspective from vacuum depositions, *IEEE J. Photovolt.* 3 (2013) 439-445.
- [6] I.L. Repins, H. Moutinho, S.G. Choi, A. Kanevce, D. Kuciauskas, P. Dippo, C.L. Beall, J. Carapella, C. Dehart, B. Huang, and S.-H. Wei, Indications of short minority-carrier lifetime in kesterite solar cells, *J. Appl. Phys.* 114 (2013) 084507.
- [7] W.K. Metzger, I.L. Repins, M. Romero, P. Dippo, M. Contreras, R. Noufi, and D. Levi, Recombination kinetics and stability in polycrystalline Cu (In,Ga)Se₂ solar cells, *Thin Solid Films* 517 (2009) 2360-2364.
- [8] S.B. Zhang, S.-H. Wei, A. Zunger, and H. Katayama-Yoshida, Defect physics of CuInSe₂ chalcopyrite semiconductor, *Phys. Rev. B* 57 (1998) 9642-9655.
- [9] S.-H. Wei and S.B. Zhang, Defect properties of CuInSe₂ and CuGaSe₂, *J. Physics and Chemistry of Solids* 66 (2005) 1994-1999.
- [10] Y. Yan, C.-S. Jiang, R. Noufi, S.-H. Wei, H.R. Moutinho, and M.M. Al-Jassim, Electrically benign behavior of grain boundaries in polycrystalline CuInSe₂ films, *Phys. Rev. Lett.* 99 (2007) 235504.
- [11] C. Persson and A. Zunger, Anomalous grain boundary physics in polycrystalline CuInSe₂: the existence of hole barrier, *Phys. Rev. Lett.* 91 (2003) 266401.
- [12] C.-S. Jiang, M.A. Contreras, I.L. Repins, H.R. Moutinho, Y. Yan, M.J. Romero, L.M. Mansfield, R. Noufi, and M.M. Al-Jassim, How grain boundaries in Cu(In,Ga)Se₂ thin films are charged: revisit, *Appl. Phys. Lett.* 101 (2012) 033903.
- [13] C.-S. Jiang, I.L. Repins, L.M. Mansfield, M.A. Contreras, H.R. Moutinho, K. Ramanathan, R. Noufi, and M.M. Al-Jassim, Electrical conduction channel along the grain boundaries of Cu(In,Ga)Se₂ thin films, *Appl. Phys. Lett.* 102 (2013) 253905.
- [14] H. Moning, Y. Smith, R. Caballero, C.A. Kaufmann, I. Lauermann, M.Ch. Lux-Steiner, and S. Sadewasser, Direct evidence for a reduced density of deep level defects at grain boundaries of Cu(In,Ga)Se₂ thin films, *Phys. Rev. Lett.* 105 (2010) 116802.
- [15] M.J. Romero, K. Ramanathan, M.A. Contreras, M.M. Al-Jassim, R. Noufi, and P. Sheldon, Cathodoluminescence of Cu(In,Ga)Se₂ thin films used in high-efficiency solar cells, *Appl. Phys. Lett.* 83 (2003) 4770-4772.

- [16] M. Nonnenmacher, M.P. O'Boyle, and H.K. Wichramasinghe, Kelvin probe force microscopy, *Appl. Phys. Lett.* 58 (1991) 2921-2923.
- [17] P. De Wolf, T. Clarysse, W. Vandervorst, J. Snauwaert, and L. Hellemans, One- and two dimensional carrier profiling in semiconductors by nanospredding resistance profiling, *J. Vac. Sci. Technol.* B14 (1996) 380-385.
- [18] I.L. Repins, C. Beall, N. Vora, C. DeHart, D. Kuciauskas, P. Dippo, B. To, J. Mann, W.-C. Hsu, A. Goodrich, and R. Noufi, Co-evaporated $\text{Cu}_2\text{ZnSnSe}_4$ films and devices, *Solar Energy Materials & Solar Cells* 101 (2012) 154-159.
- [19] I.L. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, and R. Noufi, 19.9%-efficient $\text{ZnO/CdS/Cu(In,Ga)Se}_2$ solar cell with 81.2% fill factor, *Prog. Photovolt. Res. Appl.* 16 (2008) 235-239.
- [20] I.L. Repins et al. to be published.
- [21] A. Kikukawa, S. Hosaka, and R. Imura, Silicon pn junction imaging and characterizations using sensitivity enhanced Kelvin probe force microscopy, *Appl. Phys. Lett.* 66 (1995) 3510-3512.
- [22] T. Tanaka, T. Nagatomo, D. Kawasaki, M. Nishino, Q. Guo, A. Wakahara, A. Yoshida, and H. Ogawa, Preparation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by hybrid sputtering, *J. Physics and Chemistry of Solids* 66 (2005) 1978-1981.
- [23] R.A. Wibowo, E.S. Lee, B. Munir, and K.H. Kim, Pulsed laser deposition of quaternary $\text{Cu}_2\text{ZnSnSe}_4$ thin films, *Phys. Stat. Sol. (a)* 204 (2007) 3373-3379.
- [24] Z. Zhou, Y. Wang, D. Xu, and Y. Zhang, Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ screen printed layers for solar cells, *Solar Energy Materials & Solar cells* 94 (2010) 2042-2045.
- [25] D.-H. Kuo and M. Tsega, Hole mobility enhancement of Cu-deficient $\text{Cu}_{1.75}\text{Zn(Sn}_{1-x}\text{Al}_x\text{)Se}_4$ bulks, *J. Solid State Chemistry* 206 (2013) 134-138.
- [26] C.-S. Jiang, H.R. Moutinho, R.G. Dhere, and M.M. Al-Jassim, The nanometer-resolution local electrical potential and resistance mapping of CdTe thin films, *IEEE J. Photovolt.* 3 (2013) 1383-1388.
- [27] The software is issued by ARC Photovoltaics Center of Excellence at the University of New South Wales, Australia.
- [28] L. Zhang, K. Ohuchi, K. Adachi, K. Ishimaru, M. Takayanagi, and A. Nishiyama, High-resolution characterizations of ultrashallow junction by measuring in vacuum with scanning spreading resistance microscopy, *Appl. Phys. Lett.* 90 (2007) 192103.
- [29] P. Eyben, F. Clemente, K. Vanstreels, G. Poutois, T. Clarysse, E. Duriau, T. Hantschel, K. Sankaran, J. Mody, W. Vandervorst, K. Mylvaganam, and L. Zhang, Analysis and modeling of the high vacuum scanning spreading resistance microscopy nanocontact on silicon, *J. Vac. Sci. Technol.* B28 (2010) 401-406.
- [30] M.J. Romero, H. Du, G. Teeter, Y. Yan, and M.M. Al-Jassim, Comparative study of the luminescence and intrinsic point defects in the kesterite $\text{Cu}_2\text{ZnSnS}_4$ and chalcopyrite Cu(In,Ga)Se_2 thin films used in photovoltaic applications, *Phys. Rev.* B84 (2011) 165324.

Figure Captions

Fig. 1(a) a SKPFM electrical potential, (b) a SSRM resistance, and (c) the corresponding AFM images take on the same area of the CZTSe film. GBs "A" and "B" in images (a) and (b) show higher resistance than the grain bulk, in contrast to the most of other GBs. (d) and (e) are example line profiles along the lines in (a) and (b).

Fig. 2. Sampling numbers of the low resistance channel width along the GBs, out of a total 120 GBs, showing the statistical distribution of the channel width.

Fig. 3. Calculated electron and hole concentrations around the GBs of CZTSe using grain bulk p-doping concentration of $5 \times 10^{16}/\text{cm}^3$ and GB n-doping of $5 \times 10^{19}/\text{cm}^3$. The width (25 nm) with an electron concentration larger than $1/10^{\text{th}}$ of grain bulk hole concentration is indicated.

Fig. 4(a) Change in the resistance with indentation force under a sample bias voltage of $V_s = +2$ V, (b) I-V curve taken under a large indentation force of $F = 1200$ nN.

Fig. 5(a) a SSRM resistance and (b) the corresponding AFM images taken under a small indentation force of $F = 50$ nN and a bias voltages of $V_s = 2$ V.

Fig. 6. SSRM resistance images taken under a large indentation force of $F = 1200$ nN and with (a)(b)(c) forward and (d)(e)(f) reverse bias voltages to the probe/film contact barrier.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6