



Understanding of Defect Physics in Polycrystalline Photovoltaic Materials

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Yanfa Yan

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UNDERSTANDING OF DEFECT PHYSICS IN POLYCRYSTALLINE PHOTOVOLTAIC MATERIALS

Yanfa Yan

National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, USA

ABSTRACT

The performance of thin-film solar cells is influenced by the quality of interfaces and formation of defects such as point defects, stacking faults, twins, dislocations, and grain boundaries. It is important to understand the defect physics so that appropriate methods may be developed to suppress the formation of harmful defects. Here, we review our understanding of defect physics in thin-film photovoltaic (PV) materials such as Si, CdTe, Cu(In,Ga)Se₂ (CIGS), Cu₂ZnSnSe₂ (CZTSe), and Cu₂ZnSnS₂ (CZTS) using the combination of nanoscale electron microscopy characterization and density-functional theory (DFT). Although these thin-film PV materials share the same basic structural feature—diamond structure based—the defect physics in them could be very different. Some defects, such as stacking faults and special twins, have similar electronic properties in these thin-film materials. However, some other defects, such as grain boundaries and interfaces, have very different electronic properties in these materials. For example, grain boundaries produce harmful deep levels in Si and CdTe, but they do not produce significant deep levels in CIGS, CZTSe, and CZTS. These explain why passivation is critical for Si and CdTe solar cells, but is less important in CIS and CZTS solar cells. We further provide understanding of the effects of interfaces on the performance of solar cells made of these PV materials.

INTRODUCTION

Thin-film photovoltaic (PV) modules hold great promise to produce sustainable, low-cost, clean electricity from sunlight because thin-film solar cells can potentially be fabricated by economical, high-volume manufacturing techniques. Polycrystalline Si, CdTe, Cu(In,Ga)Se₂ (CIGS), Cu₂ZnSnSe₂ (CZTSe), and Cu₂ZnSnS₂ (CZTS) have shown great potential for producing low-cost, high-efficiency, large-area thin-film solar cells, and therefore have attracted great attention for several decades [1–11]. To date, the record solar-to-electricity conversion efficiencies for CdTe, CIGS, and CZTSSe-based solar cells have reached 16.7%, 20.3%, and 9.6%, respectively [1,2,8,10]. These thin-film absorber materials share the same basic structural feature—diamond-based. Thin-film solar cells share common device structure—typically consisting of a front contact, *pn* junction, absorber layer, and back contact. However, to achieve the best sunlight-to-electricity conversion efficiency, very different fabrication processes need to be used. For example, to achieve high efficiency, Si thin-film solar cells require H passivation [2,3] and CdTe cells need heat treatment in CdCl₂ [8], whereas CIGS and CZTS solar cells do not require special passivation treatment [9,10]. Both substrate and superstrate cell structures lead to similar

performance for Si thin-film solar cells. However, the superstrate structure leads to much better efficiency than the substrate cell structure for CdTe solar cells. On the other hand, the superstrate cell structure results in better efficiency than the substrate cell structure for CIGS solar cells. It is known that the performance of thin-film solar cells depends critically on the formation of defects, including point defects, extended defects and interfaces. In this paper, we review our understanding of defects physics in thin-film solar cell materials including Si, CdTe, CIS, CZTS, and CZTSe by the combination of transmission electron microscopy (TEM) technique and density-functional theory (DFT). We find that some defects, such as stacking faults and special twins, have similar electronic properties in these thin-film materials [12,13]. However, some other defects, such as grain boundaries and interfaces, have very different electronic properties in these materials [14–20]. For example, although grain boundaries produce harmful deep levels in CdTe, they do not produce many very deep levels in CIGS, CZTSe, and CZTS.

METHOD

TEM samples were prepared by either conventional method, i.e., sandwiching two samples together, mechanically thinning them to about 2 μm, and then thinning them to electron transparency using an Ar ion beam at 6° inclination and at a liquid N₂ temperature, or by focused ion-beam technique. The samples were examined by either the conventional phase-contrast imaging technique or the high-angle annular dark-field (HAADF) imaging technique, which is also called Z-contrast imaging. A Philips CM30 microscope and FEI Tecnai F20 microscope were used. We performed the calculations using the density-functional theory, as implemented in the VASP code, with local density approximation. The energy cutoff for the plane-wave expansion was 400 eV. In all calculations, all the atoms are allowed to relax until the Hellmann-Feynman forces acting on them become less than 0.02 eV/Å.

RESULTS AND DISCUSSION

Si, CdTe, CIS, CIGS, CZTSe, and CZTS share the fundamental crystal structural feature—the basic diamond structure, as shown in Fig. 1. They can be described by the stacking of atom layers along the [111] direction. In Si, each layer contains Si atoms. For CdTe, CIS, CIGS, CZTSe, and CZTS, the layers are alternating cation and anion layers. For CIS, CIGS, CZTSe, and CZTS, the cation layers are mixed ordered cation atoms.

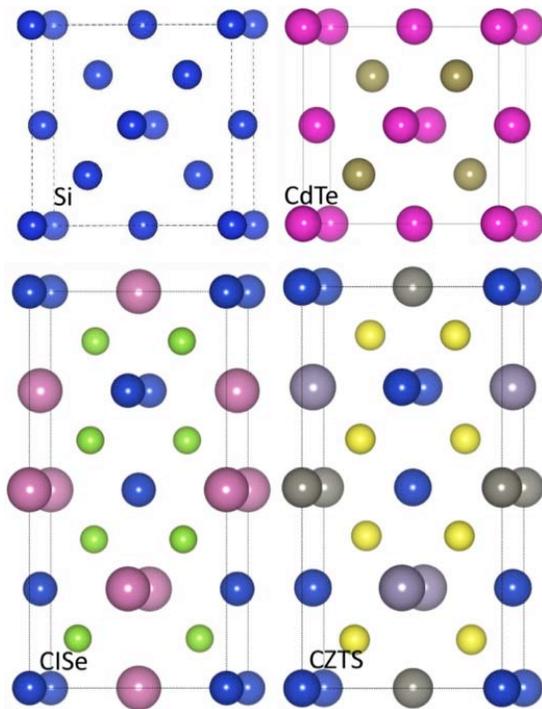


Figure 1. Structure of Si, CdTe, CIS, and CZTS.

Because of the common basic structural feature, the structure of lattice defects, such as lamellar twins, stacking faults, and grain boundaries, can be expected to be similar in these PV materials. The atomic structure of these defects in Si, CdTe, CIS, CIGS, CZTSe, and CZTS has been determined by TEM and DFT calculation [12–15]. The structure of stacking faults and lamellar twins can be described by the change of the stacking sequence. The lamellar twins have a stacking sequence of ...ABCABCACBA... An intrinsic stacking fault is where a stacking layer is removed from the perfect sequence, thus giving a sequence of ...ABCABABC... In an extrinsic stacking fault, an additional layer is inserted into the perfect sequence; thus, the stacking sequence of an extrinsic stacking fault is ...ABCABACABC... The lamellar twins and stacking faults do not have any dangling bonds or wrong bonds. Our DFT calculation on the electronic structure reveals that individual lamellar twins and stacking faults do not create any deep levels in the gap of Si, CdTe, CIS, CIGS, CZTSe, and CZTS. Thus, if separated, they are not very harmful to the electronic properties of these cubic photovoltaic materials. However, we find that high density of these defects can lead to local regions with buried wurtzite structure, which can be a barrier for the majority carriers [16].

However, the situation is very different for grain boundaries in these PV materials, even though they share the same basic structural feature. Grain boundaries generally exhibit dangling bonds, extra bonds, and wrong bonds. Figure 2 shows atomic-resolution TEM images of two grain boundaries observed in CdTe along the [110]

zone axis. The boundaries are along the (112) planes. These grain boundaries often co-exist. The experimental parameters are obtained by through-focus and through-thickness simulations of the HRTEM image of the perfect regions near the boundary. We find that the defocus value is about -65 nm and thickness is about 55 nm. Based on the obtained TEM images, structural models were constructed and optimized by DFT calculations. The atomic structures of the two grain boundaries were determined by HRTEM image simulations.

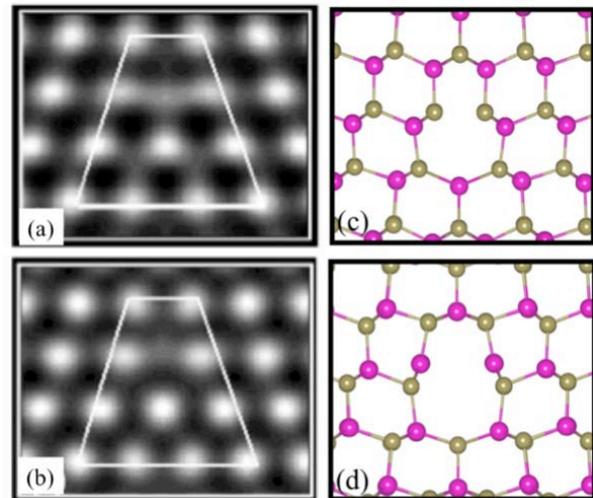


Figure 2. Atomic-resolution TEM images of grain boundaries in CdTe, (a) and (b); and their corresponding atomic structures, (c) and (d).

Figures 2(c) and 2(d) show the corresponding atomic structures. Both grain boundaries contain a dislocation core. The structure shown in Fig. 2(c) is an anion (Te)-rich structure, in which the anion atoms have dangling bonds. The structure shown in Fig. 2(d) cation-rich structure, in which the cation atoms have dangling bonds.

DFT calculations of electronic structures for these grain boundaries have indicated that the same grain-boundary structures behave very differently in these PV materials. Figure 3 shows the calculated density of states (DOS) for the anion-rich grain boundary in Si, CdTe, CIS, and CISe. Both the DOS of bulk and DOS of atoms around the dislocation cores are plotted. The arrows indicate the levels introduced by the dislocation cores. We find that the defect levels in Si and CdTe are deep in the bandgaps in Si and CdTe. However, the levels become much shallower in the bandgaps in CIS and CZTSe. We find the trend corresponds to the bonding nature in these materials. If a material has stronger covalent bonding nature, the grain boundaries create deeper gap levels. On the other hand, if a material has stronger ionic bonding nature, the grain boundaries create shallower gap levels. Our results explain why grain-boundary passivation is absolutely needed in Si and CdTe solar cells and is not so critical in CIGS, CZTSe, and CZTS.

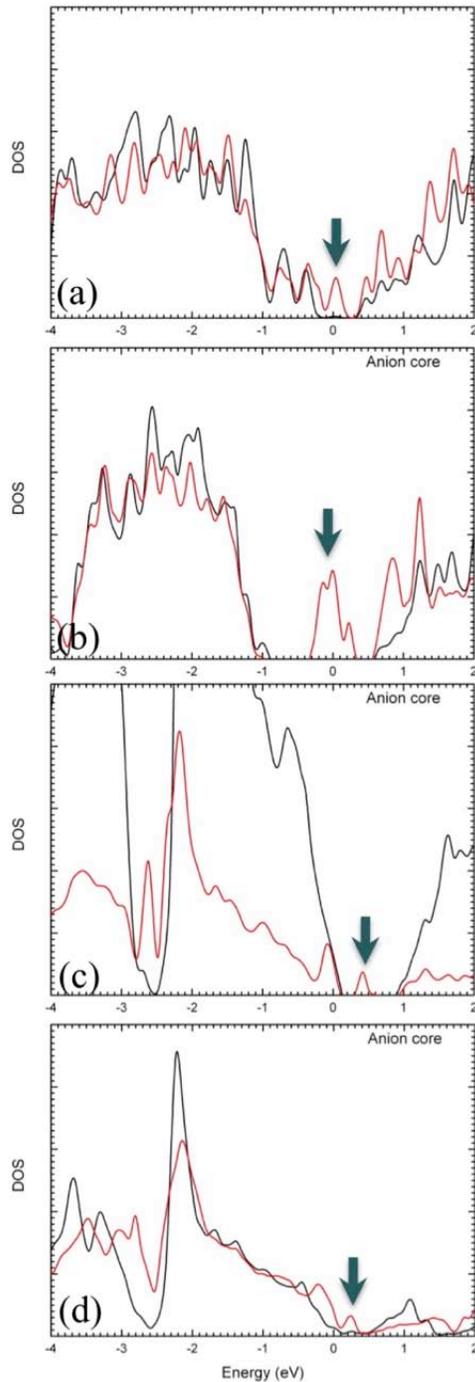


Figure 3. Calculated density of states (DOS) for the anion-rich grain boundary in (a) Si, (b) CdTe, (c) CIS, and (d) CISE.

To achieve high efficiency, a homo p-n junction is preferred. In Si solar cells, the p-n junctions are usually realized by impurity doping. In CdTe, the homo p-n junction is believed to occur through CdTe/CdS interdiffusion during CdTe deposition or CdCl₂ heat treatment. The depth of the junction should be optimized

to achieve the best performance. We found that the amount of oxygen present in the CdS layer can help to control the interdiffusion.

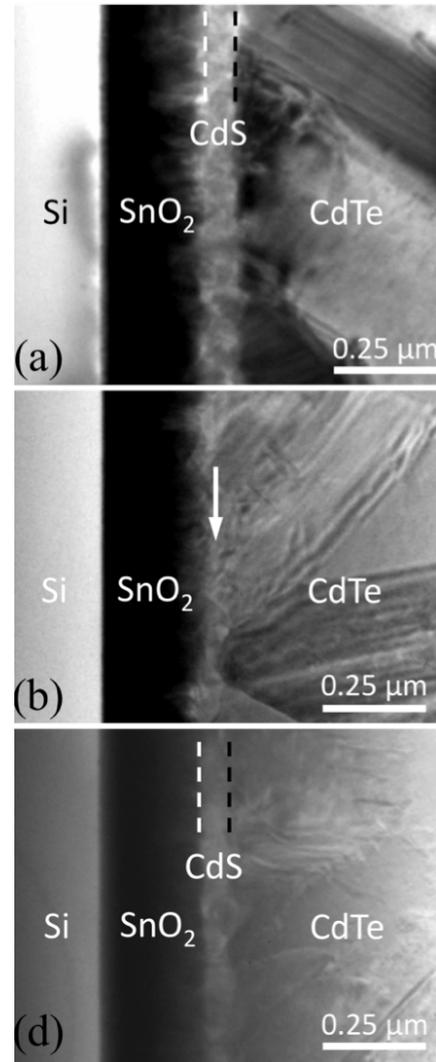


Figure 4. TEM images of (a) CdS/CdTe interface for CdS deposited with the presence of O, (b) CdS/CdTe interface for CdS deposited without the presence of O, and (c) CdS/CdTe interface for CdS deposited without the presence of oxygen, but annealed in oxygen for 10 minutes.

Figure 4 shows how the presence of oxygen in CdS can affect the interdiffusion. Figures 4(a) and 4(b) show cross-sectional TEM images of CdS/CdTe junctions with CdS films deposited with 2.5 and 0 torr O pressures, respectively. The CdS layers were about 100 nm before the deposition of CdTe. However, the CdS layer is only seen in Fig. 3(a), but is not seen clearly in some regions in Fig. 4(b). This indicates that during the deposition of CdTe at 620°C, strong interdiffusion occurred between CdS and CdTe in the sample with the CdS layer deposited without

the presence of O, and the CdS layer is consumed by the interdiffusion.

In some regions, the CdTe seems to contact directly the SnO₂ layer (as indicated by the arrow), showing a complete consumption of CdS near the junction. In some regions, the CdS layer is observed, but with significantly decreased thickness. Thus, the presence of O in the CdS layer significantly suppresses the interdiffusion at the CdS/CdTe junction. To verify this conclusion, we annealed the CSS-CdS thin film in an oxygen environment at 400°C for 10 min to incorporate oxygen into CdS. After the annealing, CdTe was deposited at the same condition. With the annealing, the CdS layer is now seen clearly, as shown in Fig. 4(c), confirming that the presence of oxygen in CdS significantly suppresses the interdiffusion at the CdS/CdTe interface.

X-ray energy-dispersive spectroscopy (EDS) taken with a small probe size of 20 nm from the thickness-reduced CdS region indicates that the CdS has converted to CdS_{1-x}Te_x alloy. In the CdTe side, CdTe_{1-x}S_x alloys were found near the junction. EDS data showed that CdS_{1-x}Te_x alloys can only be found near the junction. As the distance from the junction increases, the concentration of Te decreases rapidly. This indicates that the interdiffusion is much weaker in the CdS/CdTe junction with the CdS layer deposited with the presence of O.

In CIGS, the homo p-n junction is formed by manipulate the chemical composition at the surface, which does not require interdiffusion. The absorber layer is the 112 phase (or the α phase). However, if the composition in the surface region is tuned to be more Cu poor, which is closer to the 135 phase (or the β phase). Because the α and β phases have similar structure and lattice constants, the interface between them is coherent. Using EDS, we have determined that the surface region is indeed more Cu poor in the high-efficiency CIGS solar cells. It is known that the α phase is a p-type semiconductor and the β phase is an n-type semiconductor. So the existence of a more Cu-poor surface region leads to the formation of a homo p-n junction.

Unfortunately, the unique feature observed in CIGS does not exist in other PV materials. For example, in CZTS and CZTSe thin films, secondary phases can form easily. Figure 5(a) shows a Z-contrast image of a CZTSe thin film. The intensity variation in the Z-contrast image indicates possible formation of secondary phases, and EDS analysis indeed confirmed the existence of a secondary phase. Figure 5(b) shows the EDS obtained from the grain indicated by the square box. It shows clearly that the marked grain is Cu₂Se with very little Zn and no detectable Sn. We have also found that other phases, such as SnSe₂ and ZnS, can also form. Although ZnS is an n-type semiconductor, it would not form a homo p-n junction with CZTSe. Therefore, to form a homo p-n junction in CZTS and CZTSe, we suggest that the interdiffusion seen in the CdTe/CdS junction may be needed.

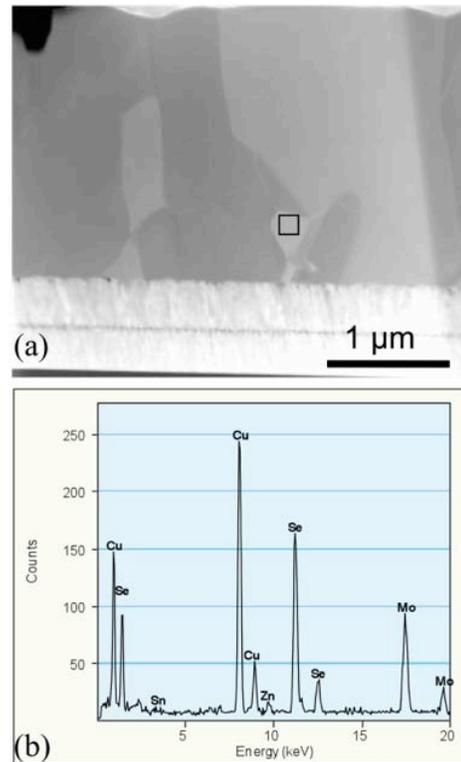


Figure 5. (a) Z-contrast image of a cross-sectional CZTSe sample. (b) EDS taken from the area marked by the square box.

CONCLUSIONS

Defect physics in thin-film PV materials such as Si, CdTe, CIGS, CZTSe, and CZTS has been analyzed using the combination of TEM characterization and density-functional theory. The same type of defect can exhibit very different effects to the electronic properties of these materials. Therefore, corresponding post-treatment and cell structure should be used to minimize the harmful effects introduced by these defects so that the cell performance can be optimized.

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