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Targeting Grain Boundaries for Structural and Chemical Analysis Using Correlative EBSD, TEM and APT

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Polycrystalline Cu(In,Ga)Se_2 (CIGS) thin-film solar cells have achieved a record efficiency of 21.7%, making them the most efficient thin-film photovoltaic device [1]. Despite the excellent efficiencies demonstrated by the technology, the overall picture of the composition related to structure at surfaces and grain boundaries (GB's) still remains ambiguous. Great efforts have been devoted to nanoscale chemical characterization of Cu(In,Ga)Se_2 thin film solar cells using atom probe tomography [2] but little correlative work has been done highlighting structure and chemistry. This contribution will discuss a novel technique used to target GB's and relate their structure to chemistry at the nanoscale. We used this technique to select from roughly 20 GB's with known misorientations, extracted from electron backscattered diffraction (EBSD) micrographs, and then chemically analyzed them in 3-D using atom probe tomography (APT). This technique may also be used for many different types of materials.

The Cu(In,Ga)Se_2 layer was grown on a Mo-coated glass using a modified three-stage process at the National Renewable Energy Laboratory. The samples were prepared for EBSD, APT, and transmission electron microscopy (TEM) analysis using an FEI Helios 600i DualBeam focused ion beam / scanning electron microscope (FIB/SEM). A cross-section of Cu(In,Ga)Se2 was prepared using the FIB, lifted out using an Omniprobe 200 nanomanipulator, and placed on a TEM grid (see Figure 1 left). A face of the sample was cleaned using a 2 kV ion beam energy to reduce damage and smooth the surface for EBSD analysis. An EBSD map was created with dimensions ~2.5 um x 2.5 um (see Figure 1 middle) on that same face of the sample. From the EBSD inverse-pole-figure (IPF) image (See Figure 1 right), a region-of-interest (ROI) was identified for APT analysis with desired GB characteristics. Next, the volume around the ROI was carefully FIB-milled, leaving a needle shaped volume containing the ROI (see Figure 2). A Philips CM200 TEM was used to capture the specimen's dimensions before and after APT using similar technique as Ref. [3], which allowed for more accurate 3D reconstructions. This was a very important step used to match the GB's found in the TEM image to the GB's found in the IPF from EBSD (See Figure 3) A final 2 kV cleaning was used to reduce the damage to approximately the outer 2 nm of the sample. APT data were collected using a LEAP 4000X Si instrument manufactured by Cameca Instruments, Inc. using laser energy of 5 pJ, a base temperature of 40K, a detection rate of 0.5%, and a laser pulse rate of 250kHz. Laser energy and base temperature were previously optimized to get equal evaporation rates of the constituent elements for a chemistry profile of the device that well represents the known stoichiometry of CIGS.

Results obtained from this new technique will also be presented (not shown) as it pertains to Cu(In,Ga)Se_2. Impurity segregation and change in matrix concentrations will be correlated to GB's misorientation [4].

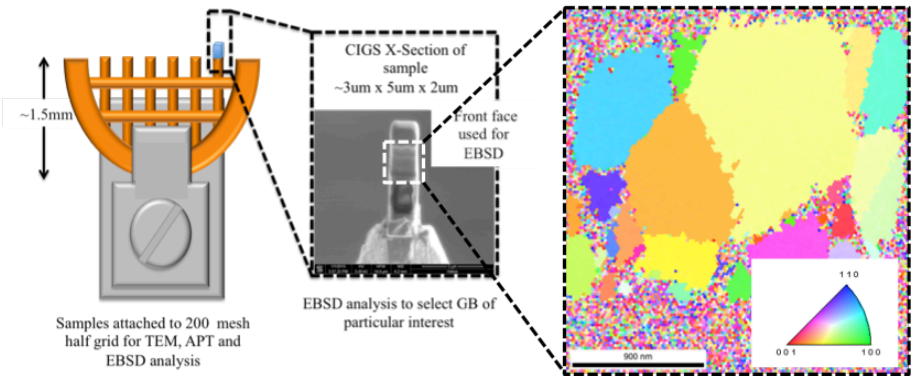

Figure 1. Left: Section of sample (blue box) sitting on TEM grid used for APT. Middle: SEM image of sample. White dashed line indicates the CIGS cross-section; the region of interest. Right: IPF of same cross-section. GB's with desired characteristics are chosen for APT analysis.

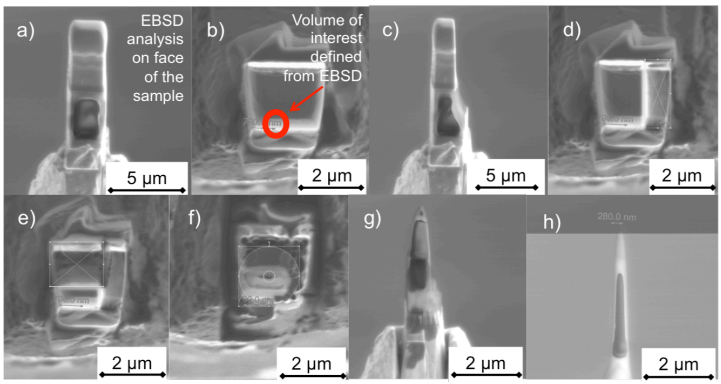

Figure 2. SEM micrographs of FIB procedure. a) Sample on TEM grid as in Figure 1. b) Top view: Desired grain boundary is beneath the red ring. c-h) Micrographs showing step-by-step FIB procedure of milling material away material except region-of-interest for APT analysis.

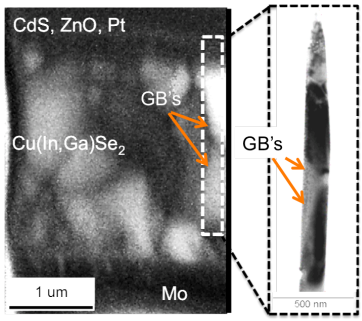

Figure 3. Image quality map from EBSD scan. TEM bright field image of atom probe tip taken from white dotted region that match GB's in both the SEM micrograph to the TEM bright field image.

References:

[1] P. Jackson et al, Phys. Status solidi- Rapid Res. Lett. Vol. 9999 (2014), p. n/a-n/a
[2] O. Cojocaru-mir et al, IEEE Journal of Photovoltaics, Vol. 1 (2011), p. 207-212
[3] K. Thompson et al, Ultramicroscopy, vol. 107 (2007) p. 131–139
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