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*Presented at the National Center for Photovoltaics and Solar Program Review Meeting
Denver, Colorado
March 24-26, 2003*



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Contract No. DE-AC36-99-GO10337

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ABSTRACT

In most Cu(In,Ga)Se₂ thin films used for solar cells, there usually exist interfaces lying about 0.1 to 0.2 μm below the surfaces. We report on a convergent-beam electron diffraction and energy-dispersive X-ray spectroscopy study of the microstructure and chemical composition of the surface region in Cu(In,Ga)Se₂ thin films. We find that the surface region and the bulk are structurally similar, with no ordered defect chalcopyrite structure observed. However, their composition is slightly different, indicating that they can have different point-defect physics. Our results suggest that the subinterfaces and the bulk absorber may form homojunctions.

Cu(In,Ga)Se₂ (CIGS) is a promising candidate for high-efficiency thin-film solar cells. The efficiency of small-area laboratory polycrystalline thin-film solar cells based on CIGS has approached 19%.¹ The four elements of this multinary polycrystalline film may form different compounds.²⁻⁴ It is known that both the conductivity type and the carrier concentration of CIGS strongly depend on the Cu/In and Se/(Cu+In) compositional ratios, which may vary in different growth processes.⁵ So far, most of the CIGS absorbers used for high-performance solar cells are grown by either the “two-stage”⁶ or “three-stage” physical vapor deposition processes.¹ In most of these CIGS thin films, subinterfaces lying about 0.1 to 0.2 μm below the surface have been observed.⁷ Because the surface layer is in the space-charge region, it may have profound effects on the cell performance. Understanding the effects is crucial for further improvements of the cell performance.

The CIGS absorber layer is a *p*-type α phase, the so-called 112 phase [Cu(In,Ga)Se₂]. The surface layer, however, was observed to have less Cu than the bulk of the film.⁸⁻¹⁰ A Cu-poor Cu–In–Ga–Se material can be either the Cu-poor α phase (chalcopyrite structure), the β phase [ordered defect (Cu vacancy, V_{Cu}) chalcopyrite (ODC) structure], or the γ phase (zinc-blende structure). A surface layer with different structures will have different electronic properties and charge recombinations, and thus, will have different effects on the junction property and cell performance. It has been assumed that the surface layer in CuInSe₂ (CIS) films has the ODC structure, the β phase, which is indicated to be *n* type. A *p*-type CIS chalcopyrite—*n*-type ODC heterojunction model has been proposed to replace the heterojunction between *p*-type CIS chalcopyrite and *n*-type CdS.⁸

However, so far, direct structural proof of the surface layer is still missing.

Here, we report on a convergent-beam electron diffraction (CBED) and energy-dispersive X-ray spectroscopy (EDS) study of the microstructure and the chemical composition of the surface layers in CIGS thin films. Having high spatial resolution, CBED is an ideal technique for investigating the microstructure of the surface layer. We find that the surface layer and the bulk are structurally similar in our samples, with no ODC structure observed. However, their compositions are slightly different (see next), indicating that they can have different point-defect physics. Our results suggest that the subinterfaces may form electrical homojunctions.

The CIGS thin films used in this study were grown by the sequential physical vapor deposition, as described in Ref. 1. Transmission electron microscopy (TEM) investigations were performed on a Philips CM30 microscope operating at 300 kV. CBED patterns were obtained with a beam size of about 60 nm.

The CIGS films were first examined using X-ray diffraction (XRD) to check the structure in the overall samples. It revealed that the thin films grown by our three-stage growth process are of the chalcopyrite α phase. None of the peaks that **are only allowed** for the defect chalcopyrite β phase were observed. Thus, XRD indicates the film contains no ODC β phase. However, it is noted that because the ODC phase may exist as a very thin layer in the surface region, the XRD data may not truly represent the structure of the surface. A technique with high spatial resolution is needed to determine the microstructure of the surface region. Also, the film’s

preferred bulk orientation is (220/204); however, the surface facets into the (112) planes (see Ref. 7).

TEM investigations revealed that the CIGS films grown by our process usually have large grains (1 to 2 μm) and low density of extended defects, such as dislocations, stacking faults, and twins. In our CIGS films, two types of subinterfaces have been observed: one is composed of dislocations, and the other consists of twin boundaries.¹¹ In many cases, the subinterface contains dislocations, but occasionally it comprises a planar defect. In some samples, subinterfaces contain a very low density of extended defects, indicating that the defects can be minimized or even eliminated by controlling the growth condition. The highest density of defects are generated at the point where the grains are growing under Cu-rich conditions. Figure 1 shows cross-sectional TEM dislocations (parallel to the film surface) that exist in the Cu-rich sample, about 0.2 μm below the surface, with the near-surface region being higher in Cu concentration.

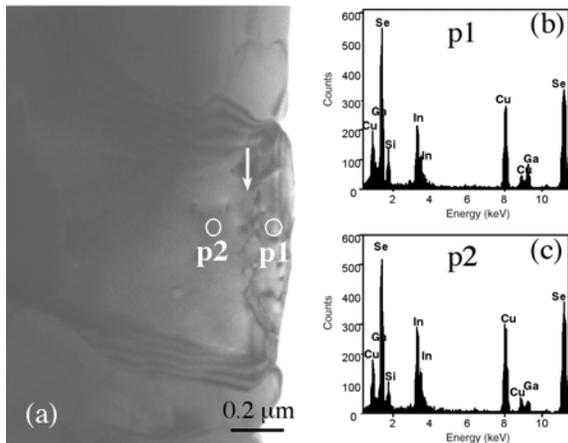


Fig. 1. (a) Cross-sectional TEM image of a Cu-rich sample, showing a subinterface near the surface. (b) EDS taken from the position p1 (between the surface and the subinterface), (c) EDS taken from the position p2 (below the subinterface).

A plan-view TEM (not shown here) shows a planar network of dislocations (see Ref. 11) in the film at this point in the growth. Figure 2(a) shows a cross-sectional TEM image of a Cu-poor CIGS film used in high-efficiency devices. The Mo layer is on the left-hand side (not shown here). It is seen that the surface region about 0.2 μm below the surface contains dislocations. The dislocation density in this film is very low. From where the dislocations disappear, the

subinterface is estimated and is indicated by the white dotted line. To examine the local chemical composition, EDS data were taken with a small probe size of 20 nm from both the surface and bulk regions.

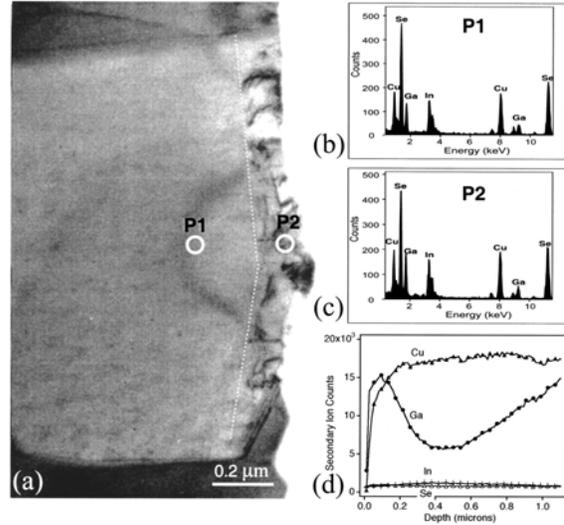


Fig. 2. (a) Cross-section TEM image of a Cu-poor CIGS film showing the subinterface. (b) and (c) EDS data taken from the bulk region P1 and the surface region P2, respectively. The subinterface is nearly edge on. (d) SIMS depth profile taken in the surface region of a CIGS film.

We found that the Cu/(In,Ga) peak ratio has a small change across the subinterface, i.e., the ratio is slightly higher in the bulk region than in the surface layer. This indicates that the surface layer is slightly more Cu-poor than the bulk regions. This is opposite of what was observed in the Cu-rich film. Figures 2(b) and 2(c) show EDS data taken from position P1 (in the bulk region) and P2 (in the surface region), respectively. The Cu/(In,Ga) ratio can be estimated by the comparison of the first Cu, Ga, and In peak intensities, which were obtained by measuring the total counts of the peaks. The $I_{\text{Cu}}/I_{(\text{In}+\text{Ga})}$ is about 0.59 for Fig. 2(b), whereas it is about 0.54 for Fig. 2(c). Thus, qualitatively, Fig. 2(c) shows a smaller Cu/(In,Ga) ratio than Fig. 2(b), indicating that the surface region is slightly more Cu-poor. The same trend was obtained from different grains and samples. This is consistent with our secondary-ion mass spectrometry (SIMS) measurements, as shown in Fig. 2(d). We measured the Cu/(In,Ga) ratios on both the surface layer and bulk regions in different grains and different samples. We find that the Cu difference between the surface region and the bulk region may vary with places, grains, and samples. In other words, the chemical composition in the surface layer varies.

Though the α and β phases have similar structure and lattice constants, the β phase has the ODC structure. The ordered structure should give extra diffraction spots in electron diffraction patterns. This allows us to identify the β phase from the α phase. Systematical zone-axis diffraction patterns confirmed that the sample has a chalcopyrite structure. Figures 3(a) and 3(b) show CBED patterns obtained from positions P1 and P2, respectively.

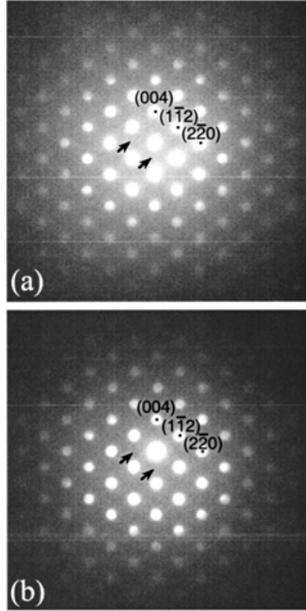


Fig. 3. CBED patterns taken from (a) bulk region P1 and (b) surface region P2.

The sample was tilted so that its $[110]$ zone axis is parallel to the electron beam. It is seen that the two CBED patterns are identical, except that Fig. 3(a) shows more inelastic diffusion than Fig. 3(b). This is because the sample is thicker at P1 than at P2. The diffraction spots can only be indexed by the chalcopyrite structure. If the surface layer is the ODC β phase, there should be extra diffraction spots at positions such as $00\bar{2}$ and $\bar{1}10$, indicated by black arrows in Fig. 3. We have taken CBED patterns with long exposure time at various places in the surface layer. However, no extra diffraction spots were observed, indicating that the surface layer is structurally similar to the absorber layer. It should be noted that their lattice constants may be slightly different due to their slightly different compositions. But the difference is beyond the accuracy limit of the electron diffraction patterns.

To support the conclusion, we examined an intentionally made very Cu-poor CIGS sample $[\text{Cu}:(\text{In,Ga}):\text{Se},1:3:5]$. In this sample, the ODC β phase is confirmed by electron diffraction. Figure 4(a) shows a selected-area electron diffraction pattern taken from this sample along the $[110]$ zone axis. The main Bragg reflections at 004 , $2\bar{2}0$, and $1\bar{1}2$ are almost the same as those seen in Figs. 3(a) and 3(b).

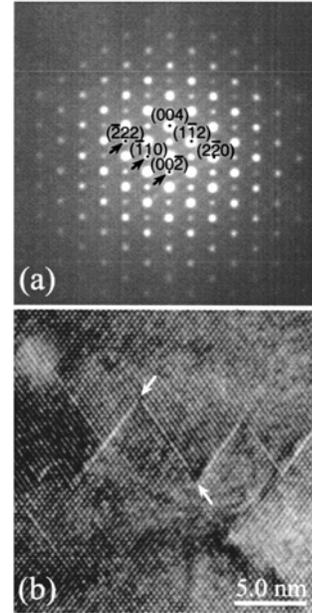


Fig. 4. CBED pattern taken from the ODC phase showing extra diffraction spots indicated by black arrows. (b) High-resolution TEM image taken from the very Cu-poor ODC phase showing $\{112\}$ domain wells.

However, additional reflections at $00\bar{2}$, $\bar{1}10$, and $\bar{2}22$ are seen, as indicated by the black arrows in Fig. 4(a), indicating that the sample is the ODC β phase. The same ordered structure has been found in very Cu-poor Cu-In-Se materials¹²⁻¹⁴ and in CuInS_2 thin films.¹⁵ Figure 4(b) shows a high-resolution electron microscopy image taken from this sample along the $[110]$ axis. As indicated by the white arrows, the sample contains zigzag domain boundaries, lying on $\{112\}$ planes. Because this sample is very Cu-poor, it should have a high density of Cu vacancies, V_{Cu} . We propose that these $\{112\}$ -oriented domain wells are formed by V_{Cu} segregation to $\{112\}$ planes.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-99GO10337.

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REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 2003	3. REPORT TYPE AND DATES COVERED Conference Paper		
4. TITLE AND SUBTITLE Microstructure of Surface Layers in Cu(In,Ga)Se ₂ Thin Films			5. FUNDING NUMBERS PVP3.3201	
6. AUTHOR(S) Y. Yan, K.M. Jones, J. AbuShama, M. Young, S. Asher, M.M. Al-Jassim, and R. Noufi				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393			8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-520-33615	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 words</i>) In most Cu(In,Ga)Se ₂ thin films used for solar cells, there usually exist interfaces lying about 0.1 to 0.2 μm below the surfaces. We report on a convergent-beam electron diffraction and energy-dispersive X-ray spectroscopy study of the microstructure and chemical composition of the surface region in Cu(In,Ga)Se ₂ thin films. We find that the surface region and the bulk are structurally similar, with no ordered defect chalcopyrite structure observed. However, their composition is slightly different, indicating that they can have different point-defect physics. Our results suggest that the subinterfaces and the bulk absorber may form homojunctions.				
14. SUBJECT TERMS CIGS; thin film; microstructure; interfaces; convergent-beam electron diffraction; energy-dispersive X-ray spectroscopy; point-defect physics; homojunction			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	