

## **Preferred Orientation in Polycrystalline Cu(In,Ga)Se<sub>2</sub> and Its Effect on Absorber Thin-Films and Devices**

M.A. Contreras, K.M. Jones, L. Gedvilas, and  
R. Matson

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# PREFERRED ORIENTATION IN POLYCRYSTALLINE $\text{Cu(In,Ga)Se}_2$ AND ITS EFFECT ON ABSORBER THIN-FILMS AND DEVICES

Miguel A. Contreras, K.M. Jones, L. Gedvilas and R. Matson  
National Renewable Energy Laboratory  
1617 Cole Blvd., MS 3211, Golden, CO 80401, U.S.A.  
phone: (303) 384-6478 fax: (303) 384-6430  
e-mail: miguel\_contreras@nrel.gov

**ABSTRACT:** The purpose of this work is to investigate physical properties of  $\text{Cu(In,Ga)Se}_2$  polycrystalline thin-films exhibiting a high degree of preferred orientation. Specifically, by using Na-free  $\text{Cu(In,Ga)Se}_2$  thin-films, it is intended to experimentally determine differences (if any) between films with a (110/102)-preferred orientation and films with a (112)-preferred orientation. The approach to the problem is a systematic comparative analysis of film and device properties in which the most significant variable is the preferred orientation of the  $\text{Cu(In,Ga)Se}_2$  polycrystalline absorbers. To complement the results of Na-free absorbers and devices, a micro-structural analysis is presented on (110)-oriented high efficiency  $\text{Cu(In,Ga)Se}_2$  absorbers ( $\eta > 18\%$ ) that are grown on standard Mo-coated soda-lime glass substrates.

**Keywords:**  $\text{Cu(In,Ga)Se}_2$  -1: preferred orientation -2: anisotropy -3

## 1. INTRODUCTION

It is a well known fact that non cubic crystal systems are in general anisotropic and that the symmetry of their physical properties are closely related to the symmetry of the crystal under consideration [1]. Given the fact that  $\text{Cu(In,Ga)Se}_2$  (CIGS) belongs to the tetragonal system, the question becomes: how much anisotropy does the system present and to what degree does it affect photovoltaic (PV) absorber material properties and consequently device performance.

In an attempt to address some of these issues, we carry out a comparative study where, to the best of our effort, the principal variable is the preferred orientation of CIGS absorbers. Specifically, we will compare some physical properties of Na-free *strongly* oriented (110/102) CIGS films and those of *highly* oriented (112) films. Additionally, we present data on high-efficiency ( $\eta > 18\%$ ) (110)-oriented CIGS films grown on standard Mo-coated soda-lime glass (SLG) as to complement the results of the Na-free films and devices

## 2. EXPERIMENTAL

Growth of CIGS absorbers is done using evaporation from elemental sources following the three-stage process developed at NREL and reported elsewhere [2]. For this experimentation, the deposition profiles for Cu, In, Ga, and Se are the same as those used in the fabrication of high-efficiency absorbers, hence, films obtained have the same composition as the high-efficiency absorbers—except for the lack of sodium—as noted later.

The substrates of choice for this experimentation are highly oriented (100) Mo foils that have been mechanically polished. After polishing, the foils are washed in a soap solution and rinsed in de-ionized water. A final plasma-cleaning step is performed to eliminate any organic materials left from the washing step.

Some of these same foils are sputter coated with a Mo layer of the same kind as used in Mo/SLG substrates. This sputtered Mo layer has a (110)-preferred orientation according to X-ray diffraction (XRD) data and is

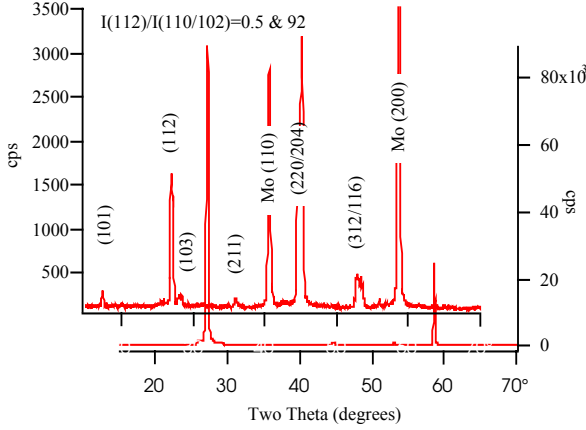
characterized by a fibrous morphology with dense and elongated grains. For more details on the properties of these sputtered Mo layers, see Ref. [3].

Each substrate used in film growth is 5 cm x 2.5 cm in size and *no sodium is incorporated* in order to eliminate it as a variable for this study. By loading both types of substrates for film growth, i.e., (100) Mo foil and sputter-coated Mo foil, in one single CIGS evaporation run, we obtain both types of CIGS preferred orientation. The (100) Mo foil substrate yields the (112) oriented CIGS whereas the sputter coated Mo foil yields the (110/102) oriented CIGS. In this fashion, we minimize—if not completely eliminate—any issues associated with composition (Cu, Ga, and Na content). *Accordingly, in every CIGS growth run, two types of preferred orientation are attained.*

We note that following a similar analysis, as presented in [4] we cannot unambiguously determine the preferred orientation of CIGS films grown on the sputter-coated Mo foil to be (110) or (102). Very likely, these films contain mostly—and among others—grains with both orientations, therefore, we refer to them as a (110/102) preferred orientation. On the other hand, we also note that the high-efficiency absorbers grown on Mo/SLG substrates are clearly and unambiguously (110) oriented.

Fig. 1 shows the XRD data for two CIGS films representative of the films used in the present work. The figure includes a measure for the degree of film orientation by taking the ratio of the measured intensities for (112) and (220/204) diffraction peaks. For comparison, we note that a randomly oriented  $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$  film has a ratio  $I(112)/I(220/204)=2.5$  (JCPDS). The Na-free (110/102)-oriented films used in this study showed ratios of intensity between  $\sim 0.4$  to  $\sim 1$ , which we consider *strongly* oriented, however, high-efficiency materials—as shown later—have intensity ratios up to 0.2, which we consider *highly* oriented. These XRD spectra were taken in a diffractometer that uses radiation from a 2-kW Cu anode and a solid state detector in the standard  $\theta/2\theta$  configuration. The preferred orientation of the films has been verified by X-ray pole-figure analysis (not shown). The pole figures indicate a uniaxial type of preferred orientation, i.e., grains are randomly oriented in the parallel

directions to the substrate plane, but highly oriented on the direction perpendicular to the substrate plane.



**Figure 1:** XRD  $\theta/2\theta$  scans for representative CIGS films with a (110/102) preferred orientation (top) and (112) preferred orientation (bottom).

### 3. RESULTS FOR SODIUM FREE CIGS ABSORBERS

In addition to the structural orientation difference, we find by scanning electron microscopy (SEM) analysis that, in general, (112)-oriented CIGS films have larger grain size morphology than those of (110/102)-oriented films. However, both types of films show significantly smaller grain sizes ( $<1\mu\text{m}$ ) as compared to films grown in standard Mo/SLG substrates. We attribute the difference to the lack of Na. The grain size difference between (112) and (110/102)-oriented CIGS films is also supported by the XRD full-width at half-maximum calculations of the (112) diffraction peaks.

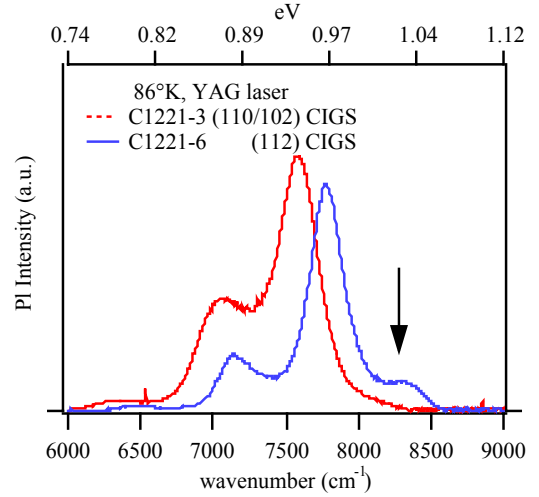
Because the films in this study are grown on conductive substrates, Hall measurements are not possible. However, simple two-probe resistance measurements (between the Mo substrate and the top of the CIGS films) reveal that, in general, the (110/102) films are more resistive than (112) films. The difference is approximately by a factor of 2 in most cases. Table 1 summarizes resistance data on representative films.

Table I: Room temperature resistance values (in  $\text{M}\Omega$ ) for oriented CIGS films on conductive substrates.

Orientation\run No.	C1221	C1227	C1277
(112)	$\sim 1.4$	$\sim 2$	$\sim 0.4$
(110/102)	$\sim 2$	$\sim 3.9$	$\sim 0.8$

Photoluminescence (PL) spectra have been obtained using a YAG laser (1064 nm, 0.21 W) at room temperature and at 86° K on several samples. In all cases, the PL spectra of the (110/102)-oriented CIGS films are shifted toward the infrared (IR). This situation suggests that (110/102)-oriented CIGS films present an *effective* lower bandgap ( $E_g$ ) value than that of (112)-oriented films. Fig. 2 illustrates this situation for one set of the samples analyzed. If the difference in  $E_g$  is estimated from the peak position

difference between the strongest emissions, the set in Fig. 2 would have an estimated 24 meV difference in  $E_g$  ( $\Delta E_g$ ). The  $\Delta E_g$  for the rest of samples analyzed ranged between  $\sim 15$  meV to  $\sim 24$  meV.



**Figure 2.** PL emission spectra for CIGS with different preferred orientation: (112) solid line (110/102) dotted line.

Additionally we note the (112)-oriented CIGS films consistently show additional transitions in the higher end of the energy spectra (see Fig. 2).

It is also interesting to note the response of both film orientations to the excitation by X-rays. Considering (a) the spectra in Fig. 1 were taken under the same diffraction conditions (generator power, beam spot size, slit size, scan step, etc.), and (b) that the samples are similar—if not identical—in composition and thickness, we note the remarkable difference in the measured intensity of diffracted beams. Namely, the (112) reflection in the (112)-oriented CIGS film has in intensity  $\sim 30$  times larger than any reflection in the (110/102)-oriented film. Because the structure, multiplicity and atomic factors implicit in XRD spectra are expected to be the same for both films, it is the *crystalline scattering factor* that becomes the reason for the difference in intensity. In other words, since X-ray diffracted beams arise from the *effective charge* (core and valence electrons) that is excited when Bragg's Law for diffraction is satisfied, the intensity of diffracted beams becomes a gauge of the effective charge density.

### 4. DEVICE RESULTS ON Na-FREE ABSORBERS

Devices were fabricated on several Na-free samples, and current-voltage (I-V) and quantum efficiency (QE) measurements were performed. In general, the I-V characteristics of devices made from (110/102)-oriented CIGS always outperformed devices made from (112)-oriented films. Significantly higher FF and lower series resistance values are in most cases responsible for the higher performance. The  $V_{oc}$  and  $J_{sc}$  values in most cases were moderately higher for the devices made from (110/102)-oriented absorbers (see Table II). Table II shows a summary of I-V parameters for selected devices. Device

data on the table are for the best cell from the sample (each sample has 6 cells).

Table II. I-V data comparison for selected devices made from absorber with a (112)-preferred orientation and from absorbers with a (110/102)-preferred orientation.

Sample/ parameter	C1121 (112)-(110/102)	C1227 (112)-(110/102)	C1277 (112)-(110/102)
$V_{oc}$ (mV)	470-462	410-454	414-502
$J_{sc}$ (mA/cm <sup>2</sup> )	33.9-35.7	22.6-28.4	34.5-37.1
FF (%)	54.9-59.0	35.8-37.4	39.3-61.3
Eff. (%)	8.7-9.7	3.3-4.8	5.6-11.4
$R_s$ ( $\Omega$ -cm)	4.80-3.57	9.57-3.57	6.42-2.69

QE data were obtained for several devices and Fig. 3 illustrates the data for a representative set. Similar to PL data above, in all cases analyzed by QE measurements the (110/102)-oriented CIGS films consistently suggest a smaller *effective* bandgap value. For instance, from data in Fig. 3 we estimate  $\Delta E_g \sim 24$  meV, which is in good agreement with the value estimated from PL data shown in Fig. 2. Other sets analyzed give a  $\Delta E_g$  as small as  $\sim 10$  meV. We ascertain that this shift in bandgap is not due to compositional variations, either on Cu content or Ga content. In reaching this observation, we had previously mapped the compositional variations of the evaporator and its effect in QE data. These compositional and QE maps allow us to fairly compare samples regardless of their positioning in the substrate holder of the evaporator.

Another important observation is that, in some cases—but not always—there is a higher collection or response in the IR for devices made from a (110/102)-oriented absorber. This situation can be observed in Fig. 3, but it is more pronounced on other samples. Considering that the compared devices were always fabricated under the same conditions (for CdS and ZnO deposition), we are unclear if such an effect is due to intrinsic differences between the absorbers, or if it is a consequence of external actions, such as the chemical bath deposition of CdS.

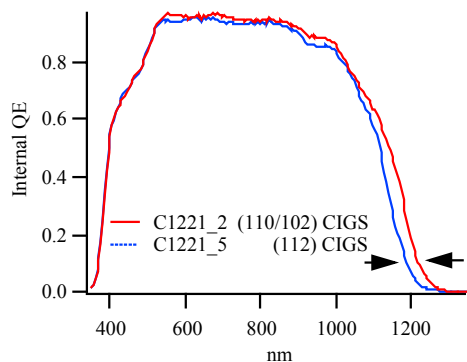


Figure 3. Internal QE data for devices made from a (110/102) oriented CIGS absorber (solid line) and a (112) oriented film (dotted line).

## 5. (110)-ORIENTED CIGS ABSORBER ON Mo/SLG

A sample (S1518) representative of high-efficiency CIGS films with (110)-preferred orientation has been prepared for transmission electron microscopy (TEM) studies. The refinement of lattice parameters for this sample from experimental XRD  $\theta/2\theta$  scans yields  $a=5.7300$  Å, and  $c=11.4090$  Å ( $c/a=1.99$ ). The same  $\theta/2\theta$  scan for this sample revealed a  $I(112)/I(110/102)=0.22$ . Because of the value of this ratio we consider this film to be *highly* oriented in the (110) direction. This sample produced several cells with total-area efficiency  $>18\%$ . The best cell in the batch had an open-circuit voltage ( $V_{oc}$ ) of 679 mV, short-circuit current density ( $J_{sc}$ ) of 35.07 mA/cm<sup>2</sup>, fill factor (FF) of 77.68%, and a total-area efficiency of 18.5% (officially measured at NREL under Global AM1.5 conditions).

Planar TEM bright-field images (not shown) on the sample reveal similar intra-grain defects as reported for In-rich CIS in the literature [5,6]. The most common planar defects observed were micro twins and stacking faults. Dislocation networks were also determined to be present in high-efficiency (110)-oriented CIGS. At this stage, we cannot determine if the density of such defects is lower in (110)-oriented CIGS, as compared to that in (112)-oriented films.

Selected area electron diffraction (SAD) performed on this material allowed us to identify (110/102)-oriented grains. Additionally, other orientations were also detected, in particular, relatively easily to find were (112)-oriented grains. Fig. 4 shows the SAD patterns from two selected grains in the sample.

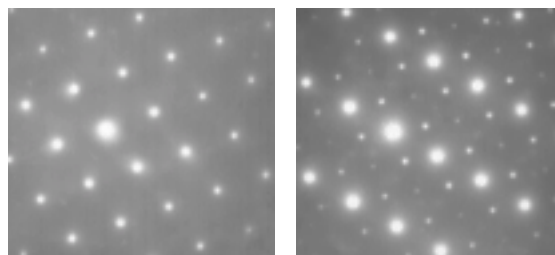


Figure 4. SAD patterns for grain with (112) orientation (left) and another grain with (110) orientation (right)

Using the calculated lattice parameters for this sample we modeled the SAD pattern for all reflections shown in the XRD pattern. In particular, we find the (110) experimental data to agree well with the modeled symmetry for the (110) surface of CIGS. On the other hand, the SAD experimental data for (112)-oriented grains agree better with a crystallite/grain undergoing a significant tetragonal distortion ( $c/a>2$ ). This situation is evidenced in the rather slanted feature to the hexagon pattern of the experimental data in Fig. 4. The modeling of SAD agrees better with a CIGS crystallite with  $c/a \sim 2.09$ , which represents a  $\sim 5\%$  increase in the value of the lattice parameter  $c$ . We attribute this *localized* change in the  $c$  lattice parameter to an elastic response to some in-plane biaxial strain.

## 6. DISCUSSION

We have established that there are some subtle yet real differences on some physical properties of CIGS films with a (110/102)-preferred orientation as compared to films with (112) orientation. Perhaps the first difference to be noted between these two preferred orientations is that (110/102)-oriented films have the *optic axis* fully exposed to incident radiation. However, in (112)-oriented films only 2/3 of the light is incident upon the optic axis (in analogy to a single crystal CIGS).

The observation of a higher resistance value on (110/102)-oriented films is noteworthy and may be related to the anisotropy in electrical transport or other defect distribution phenomena. A related observation has been made on high quality epitaxial CIGS films grown on GaAs [7]. Here, the authors report a decrease in carrier concentration—by up to a factor of 20—in highly (110)-oriented CIGS epilayers as compared to highly (112)-oriented epilayers. This observation on charge density variance is also supported (indirectly) by the XRD intensity data that suggests a lower charge density for (110/102)-oriented CIGS films.

The observation of an *apparent* smaller bandgap value in (110/102)-oriented films has also been made on CIS films grown on 7059 Corning glass by molecular beam deposition [8]. In that work, the authors suggest the lower bandgap of (110/102)-oriented films is due to a lower crystalline quality of the films with  $\text{Cu/In} < 0.88$  (smaller grain size, more defects, etc.). In our case, the (110/102)-oriented films indeed are characterized by a smaller grain size morphology as compared to (112)-oriented films—as shown above. Yet, in terms of device performance and in spite of the poorer morphology, these films present subtle (and sometimes significant) improvements over (112)-oriented films. Hence we cannot say that they are, in principle, more defective. Instead, we opt to explain the smaller bandgap in terms of the tetragonal distortion observed in high-efficiency absorbers. We know through our TEM work that (112)-oriented grains present in a (110/102)-oriented film display a relatively large tetragonal distortion ( $c/a > 2$ ). As established in refs. [8,9], such a condition would change the local value (and sign) of the crystal field splitting parameter. Since (110/102)-oriented films on average show a  $c/a < 2$  (from XRD data) the grains with  $c/a > 2$  would produce a localized upward shifting in the valence band maxima, and therefore, an *apparent* reduction in the value of the energy gap.

The observed higher QE—in some samples—in the IR (longer diffusion length) for (110/102)-oriented films is not in disagreement with the observed lower resistance (lower carrier density) on those same samples. That is, if the carrier concentration is indeed lower, a longer (deeper) depletion width can be expected—for an identical carrier concentration on the n-type side of the junction.

In general, the (110/102)-oriented absorbers lead to devices that utilize the bandgap more efficiently in terms of voltage. That is, in spite of the smaller bandgap value in those films, the  $V_{oc}$  values are always comparable—or in some cases higher—to the ones obtained in (112)-oriented absorbers. Additionally, the significantly higher FF values in combination with lower diode quality factors suggest that the main reason for the improved performance is a reduction in the space charge region (SCR) recombination.

Up to now, the discussion on devices has centered on Na-free materials, but we cannot ignore the contributions of Na to the problem of performance and preferred orientation. It is possible that with the benefits reported for Na in CIGS (enhancement in conductivity, grain-size enhancements, and others), many of the issues discussed in here will become mitigated. However, in the game to attain energy conversion efficiency beyond 20%, this work shows that all structural, electrical, optical arguments must be taken under consideration. In closing, we report that to date, all devices made at NREL with efficiency  $> 18\%$ , all show a certain degree of (110) preferred orientation.

## 7. CONCLUSIONS

We have shown that there are some subtle, yet real, differences in absorber physical properties (structural, optical and electrical) due to preferred orientation issues in Na-free CIGS absorbers. More remarkably, there are meaningful differences in device performance (namely FF values, diode quality factors and  $V_{oc}$  values) that suggest a reduced SCR recombination in devices made from (110/102) oriented CIGS films—as compared to devices built on (112) oriented CIGS. We take those results as an indication that in pursuing conversion efficiency beyond 20% all aspects of absorber and device fabrication must be taken under consideration. The changes in structural characteristics, electrical transport, optical response, etc., will undoubtedly play a role on the quality of the junctions built from such structures.

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