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*Presented at the 26th IEEE Photovoltaic
Specialists Conference, September 29–
October 3, 1997, Anaheim, California*



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A national laboratory of the U.S. Department of Energy
Managed by Midwest Research Institute
for the U.S. Department of Energy
under contract No. DE-AC36-83CH10093

Prepared under Task No. PV704301

September 1997

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ABSTRACT

The growth and characterization of Cu(In,Ga)Se₂ polycrystalline thin films under the presence of thin-MF (M=Na, K, Cs) precursor layers is presented. Some electrical, structural, and electronic absorber properties due to the presence of such Group Ia impurities are quantified along with their influence in device performance. We present a growth model for the role of Na in Cu(In,Ga)Se₂ that attributes the enhancements in electrical conductivity and photovoltaic device performance to the extinction of a finite number of donor states (i.e., In_{Cu}) at the bulk and grain-boundary regions.

INTRODUCTION

In spite of all the remarkable progress in photovoltaic (PV) CuIn_{1-x}Ga_xSe₂ (CIGS) thin films and devices, the question of the role of Na is still not completely understood. Some facts are already known, but issues that still need to be resolved are: how does Na alter parameters such as conductivity, crystallite quality [1], and device performance (particularly in extremely Cu-poor materials) [2,3]. The fundamental questions in such issues are: Is the enhancement in conductivity an *exclusive* property of Na or is it possible that similar elements (Group Ia) can produce similar effects?. Is the enhancement in conductivity due to the observed enhancement in grain size?. Does Na incorporate *substitutionally* into the CIGS lattice?. Is Na a dopant or a passivator of donor states?. How is it that Na-containing CIGS absorbers show better crystallinity and how is "better crystallinity" defined?. Our intention in this contribution is to provide some further thoughts and data on the issue and to propose a model for the role of Na in such materials. Additionally, we provide information on device performance of CIGS-absorber materials incorporating selected Group Ia (Na, K, and Cs) elements.

APPROACH AND EXPERIMENTAL

We have designed a set of experiments through which compositional, chemical, electrical, structural, and optoelectronic data have been obtained for PV-quality

CIGS materials grown on polycrystalline alumina substrates with (and without) thin-MF (M=Na, K, Cs) precursor layers. Through the above characterization, we determine whether Na incorporates substitutionally into CIGS or not. Other direct comparisons (e.g., structural, optoelectronic) between samples are performed in order to elucidate the possible role of Na in CIGS.

The CIGS films were grown by coevaporation from elemental sources using high-purity materials (usually 99.9999% purity). The substrates (alumina, 7059 Corning glass, and Mo coated soda-lime glass) were coated with thin precursor layers (~200Å) of NaF, KF, and CsF prior to CIGS growth. The 200-Å thick precursor layers provide an impurity molar concentration ~3% with respect to the CIGS layers (~2 μm thick). In a single run, four substrates (2.5 cm x 2.5 cm each) are coated simultaneously with CIGS. One piece is the control (no impurities) and the other three contain the NaF, KF, and Cs precursor layers. In this fashion, a comparison between samples from a single run is evenhanded in that all growth parameters are the same except for the presence or absence of the fluoride precursor layers.

RESULTS

Absorber Characterization

Because the Na, K, and Cs impurities are isovalent but different in ionic radii (see Table 1), the resulting electrical conductivity changes (if any) may indirectly indicate if Na incorporates substitutionally into the CIGS lattice or not. The electrical transport properties have been determined (and verified) by Hall measurements, 4-point, and thermoelectric probes. We confirmed the increase in conductivity in CIGS due to the presence of Na. The NaF-precursor layers seem very effective and usually give a conductivity increase of about two orders of magnitude. Furthermore, we establish that K produces a similar effect, but to a lesser degree. Cs, on the other hand, with the largest ionic radii (see Table 1), does not produce such an effect, and in some instances it decreases the conductivity. We have also observed that for Na, the gain in conductivity diminishes as the materials become more In rich. Indeed, as the Cu/In ratio

Table 1. Ionic radii of elements. Source: CRC Handbook of Chemistry and Physics, 68th Edition, CRC Press.

Element	Cu	In	Ga	Se	Na	K	Cs	F
A (charge)	0.96 (+1)	0.81 (+3)	0.62 (+3)	1.91 (-2)	0.97 (+1)	1.33 (+1)	1.67 (+1)	1.33 (-1)

approaches 0.5, the increase in conductivity is only about one order of magnitude. In a related study, Kohara *et al.* [4] also report a gain of about one order of magnitude for $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ materials. Fig. 1 shows the conductivity results versus Ga and Cu content. The Hall measurements (not shown) consistently attribute the increase in conductivity to a similar increase in carrier concentration. The mobility values do not seem to be significantly affected by the impurities and are usually in the 1-10 ($\text{cm}^2/\text{V}\cdot\text{s}$) range.

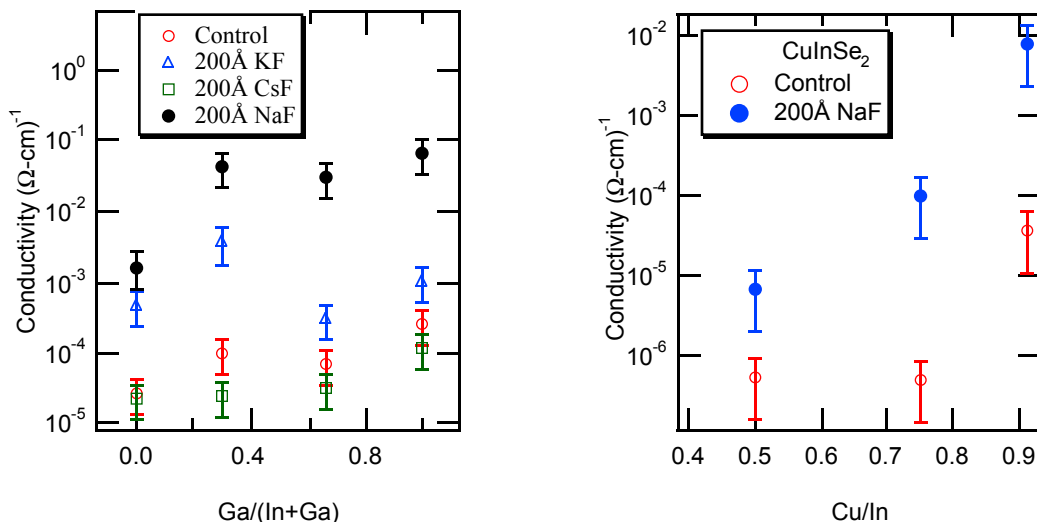


Fig. 1. Conductivity for CIGS grown on (Group Ia)F-precursor layers (left) and for CIS with NaF-precursor layers as a function of Cu content.

An interesting finding is that all precursor films led to a grain-size enhancement in CuInSe_2 (CIS) films; however, for CIGS only Na resulted in a significant enhancement of grain size. A more important observation is that there seems to be an apparent enhancement in unit-cell size with the incorporation of Na or K, but not with Cs. This is evidenced by a systematic shift of peaks toward lower 2θ values in samples containing Na (or K) (see Fig. 2). A refinement of the CIS unit cell based on the position determination of 16 XRD peaks (by a Split Pearson function) and the use of the alumina peaks as an internal reference, reveals that the Na-containing unit-cell volume is 386.49 \AA^3 and that of the control unit cell (no Na) is 385.75 \AA^3 . Such a difference becomes even larger for CIGS. For CIGS with $\text{Ga}/(\text{Ga}+\text{In})\sim 0.3$, the unit cells were calculated to be 374.25 \AA^3 and 372.92 \AA^3 , respectively.

In separate matters:

- We have learned how to grow (in Mo-coated soda-lime glass) CIGS materials with a (220) type of orientation (texture). But when such films are grown on NaF precursor layers, the texture shifts to the traditional (112) orientation.. It is not clear if this phenomenon is related to the presence of Na or if it is due to CIGS now growing on a different surface (NaF).

- Also, in samples grown with excessive Na (>400Å NaF in the precursor film), secondary phases begin to form (see Fig. 3). In CIGS absorbers with $\text{Ga}/(\text{Ga}+\text{In})\sim 0.3$, such secondary phase is characterized by three strong diffraction lines at $2\theta\sim 12.37, 24.85$ and 37.63 . Such

secondary phases are also detected in CGS. Today, all these secondary phases are unidentified, but it is likely they are some form of $\text{Cu}_u\text{Na}_v(\text{In,Ga})_w\text{Se}_z$ compound, perhaps even similar or related to phases reported/described in Refs. [5,6].

Regarding the distribution of Na, our SIMS analysis (not shown) reveals that Na segregates in the front and the back of the samples. Auger *surface* scans of CIGS materials grown with NaF show Na, O, and C, but no F. The higher the Na content, the higher the O at the surface.

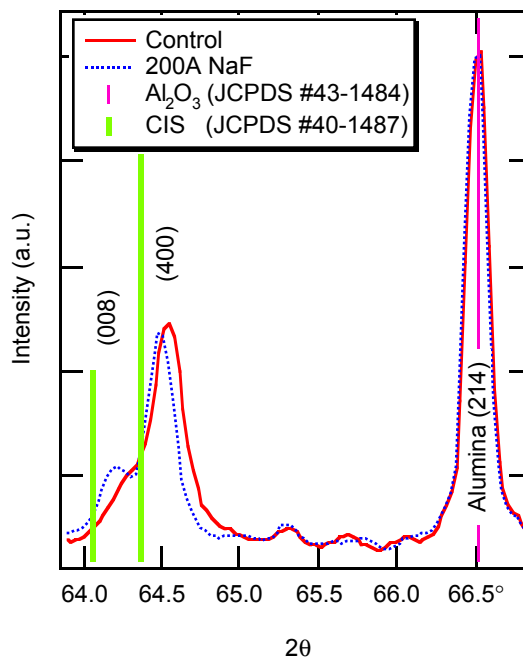


Fig. 2. XRD data for Na-containing CIS reveals a systematic shift toward lower 2θ values as compared to control samples with no impurities. Alumina peaks used as internal calibration standard.

Even though AES does not detect F at the surface, the SIMS data show that some F is present at the back of samples grown on Mo-coated soda-lime glass. A systematic XPS study of Na reveals that Na is present intragrain (bulk) and chemically bonded to Se [7].

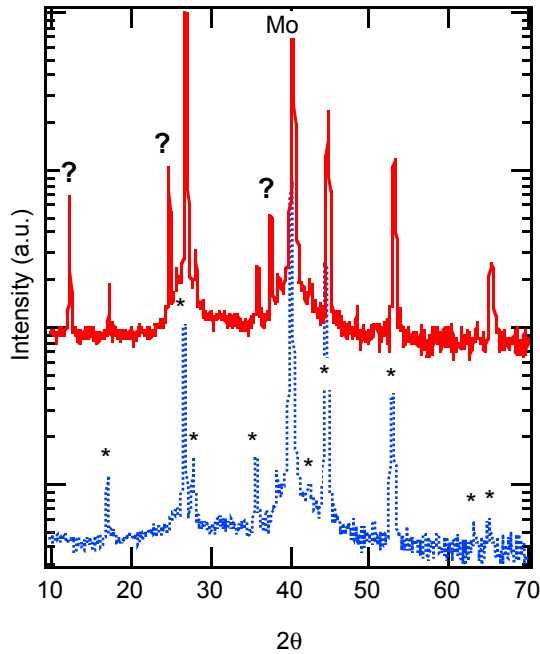


Fig. 3. XRD of CIS samples grown without NaF (bottom) and with 1kÅ of NaF (top). * indicates CIS peaks and question marks denote peaks of unknown secondary phase.

PL data have been obtained for all samples at 86 K using 0.76 mW of power from a 847-nm solid-state laser. Fig. 4 shows the spectra of three representative CIS samples. Even though the intensity units are arbitrary, the intensities can be compared between samples because excitation beam size, temperature, and power were all constants in this experiment. The spectrum for the control sample (no impurities) is similar in character to others found in the literature for related samples. The broad peaks in the CIS control sample may be a convolution of (at least) two donor-to-acceptor type transitions just as reported by authors in Ref. [8]. However, in our view the donor states stemming from In_{Cu} and V_{Se} somewhat overlap and it is difficult to tell them apart—reported ionization energies for these defects overlap [9]. Nevertheless, because: the reported formation energy of V_{Se} (2.4 eV) is higher than that of the antisite In_{Cu} (1.4 eV) [9], our compositional analysis (ICP) consistently shows Se at% to be ~50%, and recent theoretical studies [10] show that the V_{Cu} and In_{Cu} pairs are likely to be the most energetically favoured defects in CIGS, we are more inclined to assign the majority of donor levels to the antisite.

Consequently, in our argument, the high-energy transitions come mostly from donor levels (In_{Cu}) to acceptor levels (A1), whereas the most intense lower energy transitions likely come from In_{Cu} to other acceptor

levels (A2). Because the Na-containing materials become more conductive (stronger p-type conductivity), the attenuation of the high-energy transitions can be associated with a decrease in donor states, most likely In_{Cu} (and/or V_{Se}). That correlation would support the fact that the PL intensity is lower in Na-containing CIS—as compared to the control—in that, the most intense transitions are as well attenuated because of fewer In_{Cu} antisites. For the case of Cs-containing CIS samples, where the conductivity is not changed (or possibly even lowered), we observe a slight increase in PL intensity at the high end of the spectra (a possible increase in donor states, i.e., In_{Cu}). This in turn would increase the intensity in the lower energy range, as observed experimentally. The PL data obtained at 86 K have been verified at 5 K. The same features appear at this lower temperature, but with the expected shift toward higher energies due to the thermal effect on bandgap.

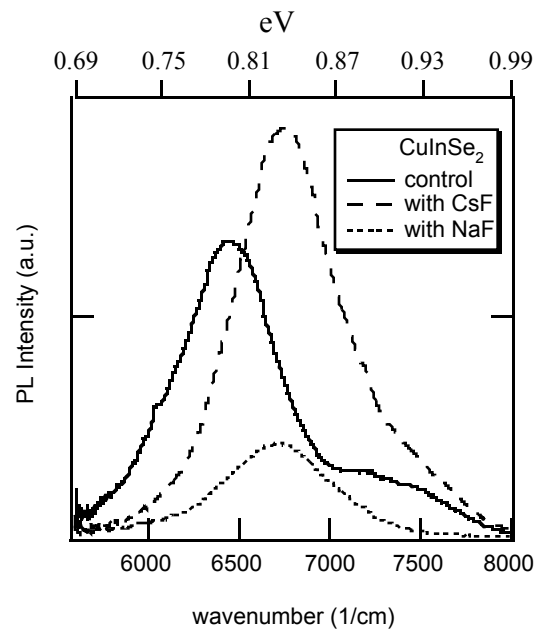


Fig. 4. PL spectra for CIS samples grown on alumina

Device Characterization

Table 2 shows a summary of I-V results for CIGS samples grown on Mo-coated alumina with (and without) the use of fluoride precursor layers. The table shows the I-V parameters for the best device (efficiency-wise) in the set.

Table 2. Summary of I-V data (1 sun, 25°C) for selected CIGS devices. The precursor layers are 200-Å thick.

Sample	V_{oc} mV	J_{sc} mA/cm ²	FF %	Efficiency %
control	520	31.2	67.2	10.9
NaF	602	30.8	72.7	13.5
KF	551	32.6	66.0	11.9
CsF	537	32.3	65.7	11.4

From C-V measurements, it is found that the introduction of Na (or K) results in an increased capacitance. The majority carrier concentration of the CIGS layer can be derived by assigning this capacitance to a free carrier population in the CIGS layer (see Fig. 5).

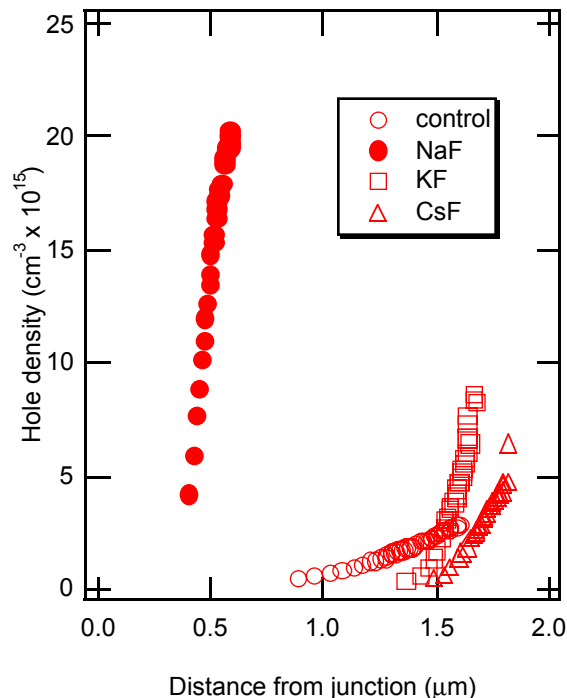


Fig. 5. Derived carrier concentrations from C-V data

The derived carrier concentration for the different samples clearly indicates that Na (and K) incorporation result in a significant increase in majority carriers relative to the control device (no impurities).

A comprehensive analysis of similar C-V data (plus DLTS) for Na-containing absorbers has been performed by Keyes *et al.* [11]. Those authors conclude that the actual increase in V_{oc} due to Na incorporation is greater than it would be expected based on the increase in carrier concentration. Thus, only some of the improvement in device performance can be explained by the increase in conductivity.

DISCUSSION AND PROPOSED MODEL FOR THE ROLE OF NA IN CIS

The XRD data indicate an increase in volume for the unit cell of materials incorporating Na (or K). From this, it seems plausible that Na (or K) can occupy *either* cation site in the CIGS lattice. From the effects of conductivity emanating from the incorporation of Group Ia impurities, we have an *indirect* corroboration that Na is incorporating *substitutionally* in the CIGS lattice. The fact that K does not yield a similar gain in conductivity is probably due to the reduced probability of K occupying either cation site. Growth of CIGS in a Cs environment does not lead to a gain in conductivity probably for the same reasons. Indeed, it is even more unlikely that Cs will occupy *any* site in the lattice. It is interesting to note that both Na and K yield increased conductivities even for CIGS materials

with high Ga contents, including $CuGaSe_2$. In other words, the increase in conductivity due to Na (or K) is independent of the Ga/(Ga+In) ratio, but it is dependent on Cu content. Because the ionic radii of Ga is even smaller than that of In, we suggest that it is unlikely that Na and K substitute for In (or Ga)—a true doping effect. Instead, we propose the incorporation of Na “annihilates” donor states, and most probably those stemming from In_{Cu} point defects. In our proposed model for the role of Na, we stipulate that during growth, when a Na and an In (and/or Ga) atom “compete” for a Cu site, it is the Na (or K) that is more likely to be incorporated at that site. Therefore, the formation of donor point-defects (In_{Cu}) is inhibited by a finite Na substitution for the In_{Cu} antisites. Hence, the net result is an increase in hole concentration. This “passivation” mechanism becomes less effective as the Cu content is reduced because in such materials the probability of forming In_{Cu} defects is increased. This explains why the increase in conductivity due to Na (or K) incorporation in extremely Cu-poor materials ($Cu/In < 0.5$) is diminished.

The strong (112) preferred orientation reported for Na-containing CIGS materials [1] can also be explained via this model. Because the <112> family of planes corresponds to the Cu and In lattice (Se excluded), it is intuitive that the “annihilation” of In_{Cu} antisites will lead to better ordering of the cations. Such ordering will result in an increase in the periodicity of the <112> family of planes and, therefore, a stronger diffraction intensity (“better crystallinity”). Also, from the above arguments, the Na concentration can be expected to be higher at grain boundaries (a pool of “passivated” donor defects), in agreement with empirical observations.

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