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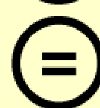

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# Alkali incorporation into solution processed CIGS precursor layers

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## Abstract

Solution based ion-exchange reactions offer a simple, non-vacuum route for adding Cu into In-Ga-Se precursor layers as a step in a low-cost process for the preparation of Cu(In, Ga)$Se_2$ (CIGS) solar cells. The chemically treated precursor layers may be converted into CIGS by annealing with Se vapour. Structural and compositional characterisation has shown that the converted layers have good composition, microstructure and crystalline phase content. Nevertheless, photovoltaic cells processed from these layers have failed to produce energy conversion efficiencies greater than ~4% under standard test conditions. The chemical bath used for the incorporation of Cu into the precursor layers includes a complexant for stability and this complexant contains alkali atoms, which are known to strongly influence the properties of CIGS. Low alkali content is highly desirable in CIGS layers but excessive inclusion may be detrimental. This paper reports the results of an investigation into the potential incorporation of excess alkali atoms from the solution into the precursor layers. Whilst no evidence of alkali incorporation is detected by energy dispersive X-ray analysis, clear evidence is seen in time-of-flight secondary ion mass spectrometry measurements. The implications of this are discussed in terms of reported effects on device performance.

## Introduction

Vacuum-evaporated, polycrystalline copper indium gallium diselenide (CIGS) thin film solar cells have reached 20% efficiency [1], however, partially non-vacuum processed devices are considered interesting despite their lower efficiencies as they have the potential for lower-cost production [2]. One potential method for non-vacuum CIGS precursor processing is the simple, non-vacuum technique of ion-exchange. It has been shown previously that Cu can be incorporated into indium gallium selenide (IGS) layers from solution via such an ion-exchange process and that the resulting precursor structure can be converted into chalcopyrite CIGS by annealing [3, 4].

Despite their dense, void-free microstructure and single phase nature, as evinced by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy, when these absorber layers are processed into solar cells energy conversion efficiencies of greater than 4.5% have not been achieved, suggesting that there may be a problem with their electronic properties.

This paper presents measurements of impurity incorporation into IGS layers during ion exchange incorporation of Cu. Time-of-flight secondary ion mass spectrometry measurements reveal that alkali ions are incorporated along with Cu ions but that oxygen, chlorine and carbon are not.

## Experimental

Indium gallium selenide layers were prepared on Mo coated soda lime glass substrates as described previously [4]. All measurements reported here were performed on a single 5 × 5cm$^2$ substrate taken from close to the mid-line of the chamber, where the thickness and composition of the IGS layers are most homogeneous. This substrate was divided into four pieces that were processed according to Table 1. All solution processing was performed at 160°C (±3°C) for 20 minutes.

| Sample | Solvent | Solute |
|---|---|---|
| 1 | Ethylene glycol | None |
| 2 | Ethylene glycol | 0.6M CuCl + 1M NaCl |
| 3 | Ethylene glycol | 0.6M CuCl + 1M KCl |
| 4 | Control, no solution processing | |

**Table 1: Sample treatment conditions, all samples were cut from a single IGS/Mo/Glass substrate.**

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to measure the compositional depth profile of the

layers. $Cs^+$ ions were used for sputtering the crater and $Bi_3^+$ ions were used for analysis. Both individual ion signals and the signals from clusters of the form ($X$ + Cs) were analysed, where $X$ is any other element. Only positive ions were detected, limiting the sensitivity of the measurements towards O, Cl and Se ions, however, positive ion clusters of the form ($X$ + Cs) would be expected to be detected in the presence of these elements. After sputtering, stylus profilometry was used to measure the semiconductor layer thickness and sputter crater depth. These two values were used to assign depths to the depth profiles, assuming different but uniform sputter rates in the semiconductor and back contact layers. The actual sputter rate in the semiconductor layer is likely to vary with the Cu concentration, however it was not possible to correct for this and so the sputter depth scale should be considered approximate. Energy dispersive X-ray analysis (EDX) measurements were performed with a tungsten filament SEM using 20keV electrons.

## Results

The ToF-SIMS ion intensities as a function of depth for the CIGS matrix elements, alkali impurities and Mo back contact are shown in Figure 1. No significant differences were observed between any of the individual ion and ion cluster signals for a given element and so the total signals are plotted to increase the signal to noise ratio. The total signals are derived by summing all of the ion signals for a given element, for example the Ga signal comprises $^{69}$Ga, $^{71}$Ga and $^{202}$(Ga + Cs).

The signals measured for samples 1 and 4 are in qualitative agreement with one another and with previous measurements on samples prepared in this manner, the oscillation observed in the In/(In + Ga) ratio is explained by the source geometry [4]. There is some difference between the Na signals in the two samples, though the mean signal is very similar and so the difference is attributed to the higher noise recorded from sample 4.

The samples treated in Cu solutions both show Cu signals peaking at the surface and decaying into the depth of the layer. In both cases the In and Ga signals decrease at the surface and tend towards their initial values deeper in the layer. Cu ions are highly mobile in CIGS and strongly susceptible to forward sputtering effects, therefore it is often difficult to establish where the true Cu signal ends and the signal due to forward-sputtered ions begins to dominate. However, the ratio [Ga]/([In]+[Ga]) provides some additional evidence in this case as it has been shown previously that In participates in the exchange reaction more rapidly than Ga and so [Ga]/([In]+[Ga]) will be increased in the presence of Cu [4].

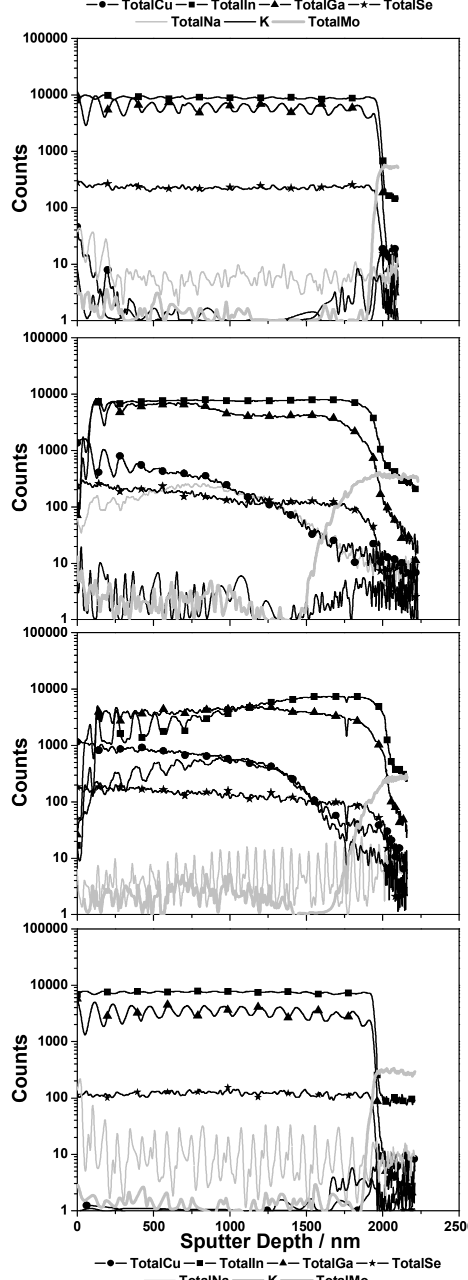


**Figure 1: ToF-SIMS ion intensities as a function of depth showing the Mo back contact, CIGS matrix elements and alkali impurities. The samples processed in solutions containing alkali complexants show enhanced alkali signals, indicating incorporation of alkali cations into the layers.**

Accordingly, it is seen that the exchange reaction appears to have progressed further for sample 3 than for sample 2, an observation that is in agreement with the EDX signals measured from these samples. Both samples 2 and 3 show strong enhancement of the signal corresponding to the alkali species used in the

ion-exchange bath, indicating that these ions are incorporated from the bath. The alkali signals begin to fall off at the same position as the Cu signal, however, they peak just before this region, rather than at the surface as is the case for the Cu signal.

EDX measurements were made to try and establish limits on the level of alkali ion incorporation into the precursor layers. Due to the graded compositional depth profile of the precursors, accurate quantitative composition measurement is not possible with EDX since only the upper part of each layer is sampled by the electron interaction volume and the composition is inhomogeneous through the depth of this volume. Figure 2 shows sections of the EDX spectra measured from samples 2 and 4, centred near the position expected for the NaK peak. For comparison, four spectra are included that were measured from a mixture of CuCl and NaCl powders, they are shown normalised to have the same CuL count as the measurement on sample 2.

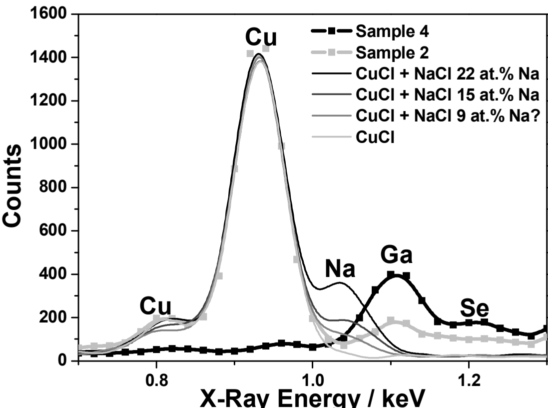


**Figure 2: EDX spectra measured from samples 2 and 4 and from a mixture of CuCl and NaCl. No evidence of Na incorporation is seen in the EDX spectrum of sample 2.**

The NaCl powder was much coarser than the CuCl powder and so it was possible to vary the quantity of NaCl included in the measurement by adjusting the measurement region. As the amount of NaCl included in the measurement was decreased, the Na peak reduced in area. By the time the quantisation routine indicated 9 at.% Na in the measurement, a small shoulder on the CuL peak was still visible, however removing Na from the elemental quantification made no difference to the calculated accuracy of the fit. Therefore, it is concluded that the quantisation algorithm is already unreliable below approximately 10 at.% Na for the powder mixture. The situation is made more complex by the presence of the GaL peak on the high-energy side of the NaK peak and therefore, even though EDX is normally quoted as having sensitivity and accuracy around 1 at.%, it is considered probable that it may be unable to detect several at.% Na in these samples. For the measurement of sample 2, there is no evidence of a shoulder on the side of the CuL peak where the NaK peak would be expected, suggesting Na incorporation well below 10 at. %.

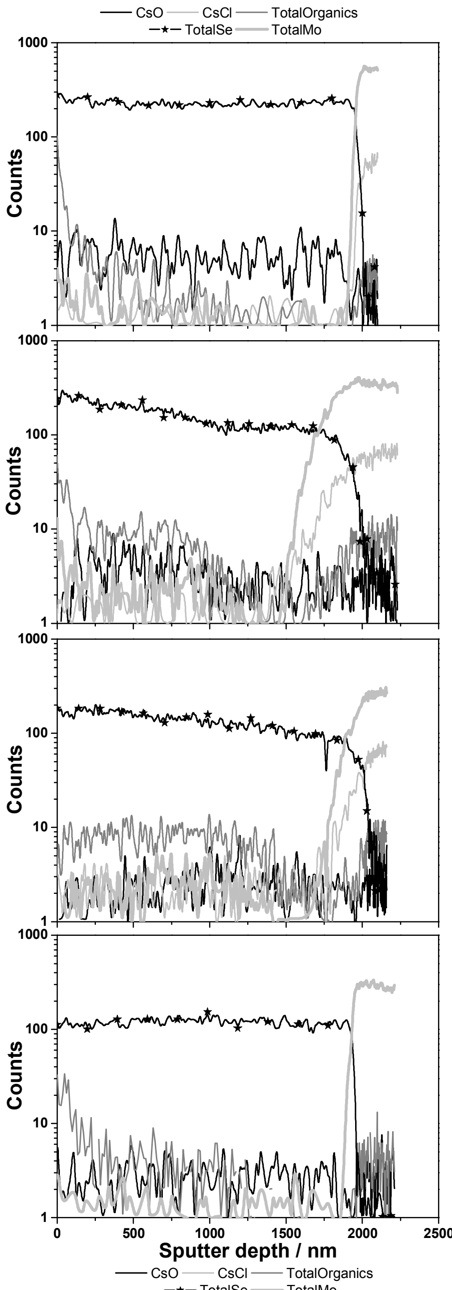


**Figure 3: ToF-SIMS ion intensities as a function of depth for the impurities considered most likely to be incorporated into the layer during solution processing. The Se and Mo back contact signals are shown to indicate the position of the impurity signals relative to the precursor layer.**

Figure 3 shows the ion intensities as a function of depth for the impurities considered most

likely to be incorporated into the layer during solution processing. The total organic signal includes a range of C—H compounds as well as (C + Cs) and it peaks at the surface due to contamination during sample handling. The oxygen and organics signals are comparable to the noise level on the measurements and remain unchanged across the IGS-Mo boundary, indicating that there is no oxygen or C contamination in the layer. The (Cl + Cs) signal is also comparable to the noise level, however it increases in line with the Mo signal at the rear interface. This is assigned to a mass overlap between (Cl + Cs) and (Mo + *X*), where the mass, *m*, of *X* is $68 \leq m \leq 76$, though it is unclear what ion or ion cluster this could be.

## Discussion

Limited chemical and physical data on alkali selenide compounds are available and combined with the uncertainty in the phase composition of the IGS precursors, this makes identification of the alkali incorporation route difficult. Two potential mechanisms may, however, be proposed. Firstly, the alkali ions may diffuse into vacancies in the IGS layer, such vacancies would be expected due to the disordered nature of the mixed phase layers and the defect-wurtzite structure of any $In_2Se_3$ phases present. However, this would require that the ions be reduced at some point to avoid accumulation of charge on the precursor layer. Secondly, the alkali ions may participate in an ion exchange reaction in the same manner as the Cu ions. Since the peak alkali concentration is observed to lie midway through the layer rather than at the surface the following three (unbalanced) reactions are proposed to occur in parallel, with the latter happening more slowly than the former two:

1) In-Ga-Se + $Na^+$ -> Na-Se + $(In, Ga)^{3+}$
2) In-Ga-Se + $Cu^+$ -> Cu-Se + $(In, Ga)^{3+}$
3) Na-Se + $Cu^+$ -> Cu-Se + $Na^+$

Typically, PV devices processed from these precursors exhibit very low $V_{oc}$ and parallel resistance values and though their rough surface morphology may explain some of the loss in these values as compared to high efficiency devices, it is considered unlikely to account for all of it. Whilst quantisation of Na incorporation was not possible with the measurements performed here, previous work has indicated that any extra Na incorporation above that which diffuses from soda lime glass is detrimental to cell quality [5, 6]. Therefore, the detected alkali incorporation offers a potential explanation for the poor performance of the devices as it will be in excess of the Na expected to diffuse into the layers from the glass during high temperature selenization. It has been suggested that such excess Na can lead to $NaInSe_2$ secondary phases as well as prevent the formation of the $CuIn_3Se_5$ surface phase that is considered desirable for heterojunction formation [7] and measurements of cells produced with excess Na showed significant reductions in $V_{oc}$ [6, 8], consistent with devices processed from these precursors. The loss of $V_{oc}$ is reported as possibly due to the formation of a high density of deep trap states [9].

A complexant is required in the ion-exchange bath to maintain its stability and molecular ligands such as ethanolamines might be suitable replacements for the alkali salts used so far, however they have yet to be tested.

## Conclusions

A possible explanation for the poor performance of CIGS devices containing ion-exchanged precursor layers has been identified as the incorporation of excess alkali atoms during chemical processing. Further work is required to test this hypothesis by adjusting the chemistry of the ion-exchange bath to avoid the use of alkali atoms.

## References

[1] Repins I, Contreras MA, Egass B, DeHart C, Scharf J, Perkins CL, To B, Noufi R. *Progress in Photovoltaics Research and Applications* 2008; **16 :** 235-239.
[2] Kaelin M, Rudmann D, Tiwari AN. *Solar Energy* 2004; **77 :** 749-756.
[3] Hibberd CJ, Ernits K, Kaelin M, Muller U, Tiwari AN. *Progress in Photovoltaics: Reasearch and Applications* 2008; **16 :** 585-593.
[4] Hibberd CJ, Ganchev M, Kaelin M, Dann SE, Bilger G, Upadhyaya HM, Tiwari AN *Thin Solid Films* 2009; **517 :** 2235-2239.
[5] Rockett A. *Thin Solid Films* 2005; **480-481 :** 2-7.
[6] Rockett A, Britt JS, Gillespie T, Marchall C, Al Jassim MM, Hasoon F, Matson R, Basol B. *Thin Solid Films* 2000; **372 :** 212-217.
[7] Wei S, Zhang SB, Zunger A. *Journal of Applied Physics* 1999; **85 :** 7214-7218.
[8] Granata JE , Sites JR. *26th IEEE Photovoltaic Specialists Conference,* Anaheim, USA 1997; 387-390.
[9] Rau U, Schmitt M, Engelhardt F, Seifert O, Parisi J, Riedl W, Rimmasch J, Karg F. *Solid State Communications* 1998; **107 :** 59-63.