The Importance of Se Partial Pressure in the Laser Annealing of $CuInSe_2$ Electrodeposited Precursors

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***ABSTRACT* — One method for producing $CuInSe_2$ (CISe) absorber layers is electrodeposition followed by annealing. Replacing the commonly used furnace annealing step with a laser can reduce annealing times by 2-3 orders of magnitude: from 30 minutes to 1 s. However, laser processing has, to date, not resulted in absorber layers which can form functioning final devices. One reason is due to Se loss during annealing even on these short timescales. We show how this Se loss is reduced by using a background partial pressure of Se (P_{Se}) during annealing. Higher P_{Se} results in increased grain size and drastically increased photoluminescence yield. The introduction of an elevated P_{Se} in the laser annealing chamber enabled the fabrication of the first known $CuInSe_2$ photovoltaic device using electrodeposition followed by laser annealing which gave 1.6% efficiency.**

***Index Terms* — annealing, lasers, photovoltaic systems, thin films, X-ray diffraction.**

I. Introduction

$Cu(In,Ga)Se_2$ is an important absorber layer for thin film solar cells with a record reported power conversion efficiency of 20.8% [1]. One $CuInSe_2$ (CISe) fabrication route uses a two-stage process: deposition of a precursor followed by annealing. Whilst vacuum deposition methods have, to date, resulted in higher efficiency devices, electrodeposition of precursors offers advantages as it is carried out under ambient temperatures and pressures and is highly resource efficient. Annealing is commonly carried out using a furnace where the precursor is heated to temperatures of 400 – 600 ^oC for 30 – 60 mins under a Se atmosphere. Replacing the furnace with a laser can reduce this annealing time by 2-3 orders of magnitude. However, previous attempts at laser annealing electrodeposited CISe have not produced material suitable for devices; secondary phases remain [2] and the absorber layers have been observed to melt in the high annealing temperatures [3]. In past work, we have shown that laser annealing co-electrodeposited precursors with a Nd:YAG, continuous wave (CW) laser (λ = 1064 nm) at powers from 50 – 1000 Wcm^{-2} for 0.5 – 60 s resulted in CISe absorber layers with evidence of improved crystallinity and optoelectronic properties over the precursor [4]. Whilst an absorber layer from this process was completed into a device showing diode behavior, its efficiency was negligible.

A key observation of this past work was that even laser annealing with a dwell time of 1 s or less resulted in Se loss from the precursor. The release of Se from the precursor may result from the breakdown of the CISe, as detailed by Scragg et al. [5], into its binary selenides or metallic elements. Furthermore a Se/(Cu+In) < 1 can be linked to an increase in parasitic defects such as In_{Cu} and V_{Se} [6]. The presence of these defects and secondary phases in an absorber layer is expected to impair device efficiency.

One method of preventing Se loss, as used in furnace processes, is by the presence of a Se atmosphere during annealing. A background partial pressure of Se (P_{Se}) exceeding the equilibrium vapor pressure of the CISe decomposition reactions [5], renders Se loss via these routes thermodynamically unfavorable. In addition, grain growth and the improvement of optoelectronic properties are linked to the background pressure of Se [7].

Here we test the effect of varying P_{Se} during the laser annealing of electrodeposited CISe, on the composition, crystallinity and optoelectronic properties of the resulting absorber layers, which we hypothesize to improve with increasing Se activity.

II. Experimental

$CuInSe_2$ precursors were formed by co-electrodeposition of the elements Cu, In and Se. The aqueous electrolyte was composed of 2.56 mM $CuCl_2.2H_2O$ (99.999 %, Alfa Aesar), 2.4 mM $InCl_3$ (99.99 %, Alfa Aesar), 4.9 mM H_2SeO_3 (99.999% Sigma Aldrich), 0.24 M KCl (99.999 % Sigma Aldrich), 10 mM H_3NSO_3 (99.999 % Sigma Aldrich), and 10 mM $C_8H_5KO_4$ (≥ 99.95 % Sigma Aldrich). A substrate of soda lime glass sputtered with Mo was suspended horizontally in the plating bath to form the working electrode. An Ag | AgCl reference electrode and large-area Pt counter electrode

completed the electrochemical cell. Deposition time was calculated to give a film thickness of 1 μm. This deposition results in Se rich films (Se/(Cu+In) = 1.3 – 1.4).

Laser annealing was carried out using a Nd:YAG laser (λ = 1064 nm) in continuous wave (CW) mode. The beam was collimated and passed through a 2 x 2 mm aperture, giving this approximate spot size on the sample. The samples were annealed by rastering the laser beam with average flux of 150 Wcm^{-2} (Gaussian spreading function 1/e = 1.9 mm) across the sample surface at 2 mms^{-1}, i.e. ≈ 1 s dwell time. Prior to annealing, each precursor piece was mounted into a small volume annealing chamber. The chamber is sealed apart from valved inlets and outlets to allow for control of the atmosphere. Firstly, the chamber was purged with Ar and then a controlled Se atmosphere created. The P_{Se} utilized in this work are as follows: 9 x 10^{-7} Pa (lowest: (i)), 4 x 10^{-5} Pa (low (ii)), 1 x 10^{-3} Pa (high (iii)), and 2 x 10^{-2} Pa (highest (iv)). To ensure consistency in precursor composition and uniformity, these annealing experiments all relate to a single symmetrical CISe precursor film which had been split into four pieces.

In order to assess the effect of P_{Se} during annealing, the structural and optoelectronic properties of the precursor and absorber layers were examined. Morphology and composition were determined using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) on a combined Hitachi SU 70 system. Crystal structure was determined using x-ray diffraction (XRD) on a Pananalytical X'pert Pro system with Cu Kα radiation in θ-2θ configuration.

Before optoelectronic analysis, laser annealed absorber layers were etched with 5 wt% KCN for 30 s and then coated with a 50 nm layer of CdS deposited by chemical bath deposition. Room temperature photoluminescence (RT-PL) measurements were achieved, using excitation from a semiconductor laser at λ = 660 nm and an InGaAs detector.

In order to understand the effect of P_{Se} on device efficiency, a second, similar, electrodeposited precursor was split into two pieces and laser annealed. The absorber layers were completed into final devices by etching with 5 wt% KCN for 30 s and immediately coating with 50 nm CdS; followed by sputtering ZnO window layers onto the surface and scribing 3 x 3 mm cells. Current voltage (IV) measurements were carried out at room temperature under AM1.5 illumination.

We emphasize that all structural and optoelectronic improvements shown in this work were achieved with only a single second annealing time.

III. Results and Discussion

A. Structural Properties

To understand the influence on the structural properties of CISe absorber layers of the background P_{Se} during the laser annealing, XRD diffractograms were measured on absorber layers annealed under P_{Se} = (i) – (iv). In order to compare the relative difference in crystal coherence lengths the full width at half maximum (FWHM) of the CISe 112 peaks are determined using the Scherrer formula. The calculated coherence length ('*D* parameter') is compared to cross section appearance as shown in Fig. 1.

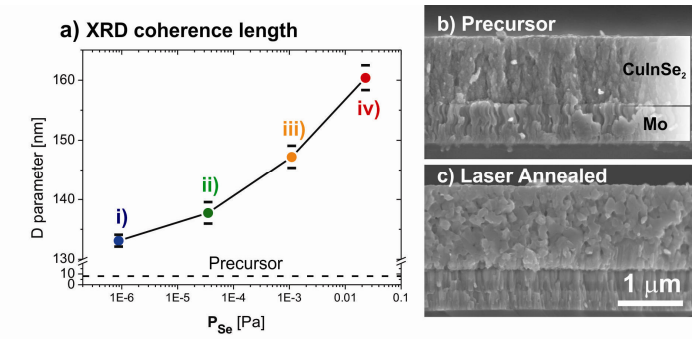

Fig 1. a) Coherence lengths as determined from the FWHM of the CISe 112 peak of XRD diffractograms of electrodeposited precursors which have been laser annealed at 150 Wcm^{-2}, 2 mms^{-1} under background P_{Se} = (i) – (iv). These are compared to the precursor. SEM cross section micrographs of b) electrodeposited precursor and c) laser annealed sample (i).

Figure 1a) shows that laser annealed absorber layers (i – iv) have a larger *D* parameter (i.e. a narrowing of CISe peaks in XRD diffractogram) compared to the nanocrystalline precursor. Furthermore, there is a positive correlation between P_{Se} and the *D* parameter. This would indicate that a higher P_{Se} during laser annealing results in larger coherent domains within the CISe absorber layer. This may relate to the removal of structural defects and/or an improvement in crystallinity. Evidence for an increase in grain size is visualized in the SEM micrographs, where the small grains of the precursor (Fig. 1b) become larger and more angular after annealing (Fig. 1c). This larger grain size reduces the surface area of grain boundaries where recombination is possible, thus is expected to lead to an improvement in the photovoltaic properties of a device.

B. Optoelectronic Properties

Past work of laser annealing under an inert atmosphere indicated that even during the 1 s annealing time, Se loss from the sample was significant [4]. The loss of Se during annealing may result in the formation of defects and secondary phases [5,6] and therefore is expected to be the primary cause of the observed poor optoelectronic performance. To investigate whether by having an elevated background P_{Se} this Se loss can be reduced, the absorber layer composition (determined by EDX) was compared to the background P_{Se} during laser annealing the results of which are shown in Fig. 2.

In Fig. 2 it is seen that the precursor has Se/(Cu+In) = 1.36, a value significantly above stoichiometry. This high Se content may indicate that it contains elemental Se, which is expected to vaporize during annealing. This is supported by all absorber

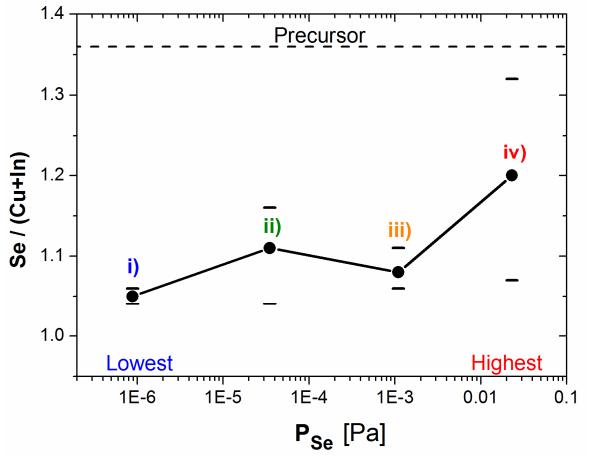

Fig. 2. Average Se/(Cu+In) composition, measured using EDX, of the electrodeposited CISe precursor and after laser annealing at 150 Wcm^{-2}, 2 mms^{-1} low to high (i – iv) P_{Se}. This average was taken by measuring three different points on the same sample and error bars indicate the maximum and minimum values observed.

layers having a reduced Se content compared to the precursor, although Se/(Cu+In) remains > 1 in all samples. This unusually high value may relate to the presence of the $CuIn_3Se_5$ phase at the sample surface, as has been observed previously [4]. With increasing P_{Se}, a higher average Se/(Cu+In) is measured in the absorber layer after laser processing. From these results it is concluded that increasing the background P_{Se} reduces Se loss during annealing. Se loss is believed to be via decomposition of the CISe [5]. This not only reduces the volume of CISe semiconductor material, but also leads to the formation of binary selenides. Comparing the equilibrium partial pressures of the CISe decomposition reactions (given in ref. [5]), indicates that a background P_{Se} > 2 x 10^{-3} Pa (at 550 ^{o}C) results in these reactions becoming thermodynamically unfavorable. On this basis, the breakdown of CISe is thermodynamically favorable in all but the 'highest' Se activity (P_{Se} = 2 x 10^{-2} Pa), assuming that the peak film temperature during laser annealing exceeding 550^{o}C.

To determine if an increased Se content in the absorber layer leads to an improvement in its optoelectronic properties, RT-PL measurements were made, the results of which are shown in Fig. 3.

The electrodeposited precursor is seen in Fig. 3a) to give a very weak PL signal within the measured range. As CISe has a band gap: $E_g \approx 1$ eV, the low PL yield indicates the absence of high quality semiconductor material within this energy range. After laser annealing there is an increase in the PL yield. The PL yield increases in conjunction with larger P_{Se} as can be clearly observed in Fig. 3b). An increased PL yield relates to a higher level of radiative recombination, which can be correlated to the final V_{oc} of a device. Only the absorber layer annealed under the highest P_{Se} (iv) gives a single peak in PL intensity around 1 eV, assumed to relate to band to band transitions. At lower P_{Se} the absorber layers show a second increase in intensity at lower energies indicating transitions within the band via defect states, or secondary phases. This supports the hypothesis that the background P_{Se} reduces decomposition of the CISe, and reinforces that only the highest P_{Se} is sufficient to prevent material breakdown.

A second set of precursor films were laser annealed under 'lowest' (9 x 10^{-7} Pa) and 'medium' (2 x 10^{-4} Pa) P_{Se} and the absorber layers were completed into solid state devices. Whilst that annealed under the 'lowest' P_{Se} showed no diode behavior, the one from the process with 'medium' P_{Se} gave 1.6 % power conversion efficiency [8]. To our knowledge this is the first working device formed from the electrodeposition-laser annealing process.

To summarize, we have shown that by increasing P_{Se} during laser annealing, the structure and optoelectronic properties of the resulting absorber layers are improved. The poor optoelectronic properties after annealing with an insufficient background P_{Se} are related to the formation of V_{Se} defects and/or decomposition of the CISe semiconductor. By using an elevated P_{Se} during laser annealing, absorber layer properties are improved sufficiently to form a final device giving 1.6 % efficiency.

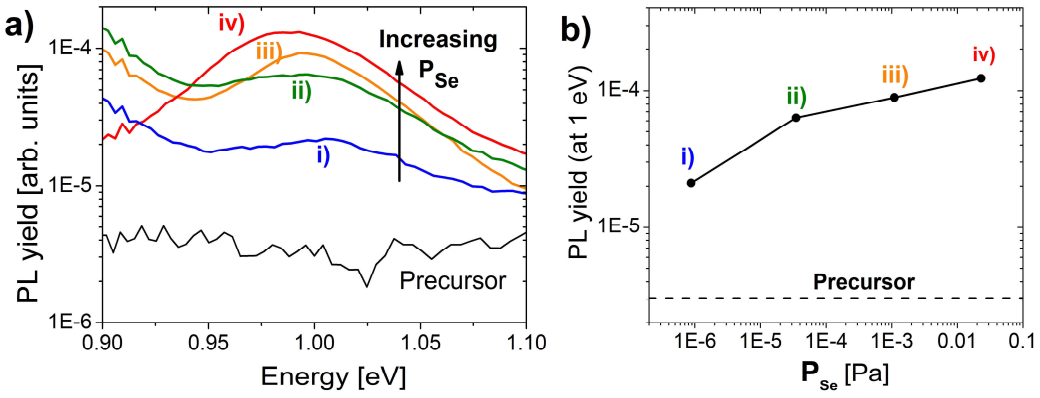

Fig. 3. a) RT-PL spectra of the electrodeposited CISe precursor and after laser annealing at 150 Wcm^{-2}, 2 mms^{-1} samples with low to high (i – iv) P_{Se}. b) PL yield at 1 eV for samples detailed in (a).

IV. Summary and Conclusions

We have thus shown how the background P_{Se} during 1 s of laser annealing, influences both the structural and optoelectronic properties of the resulting absorber layers. The significance of these findings are confirmed by only being able to form a functioning device once an adequate P_{Se} is present during the annealing process. Hence we validate an absorber layer fabrication method that enables the laser annealing of electrodeposited CISe with only 1 s dwell time. The fabrication of these absorber layers into functioning photovoltaic devices means the optimistic view-point of development of this technique into a rapid industrial fabrication process is founded.

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