Comparative study of laser induced breakdown spectroscopy and secondary ion mass spectrometry applied to dc magnetron sputtered as-grown copper indium diselenide (CIS)

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Abstract

The University of Salford has led the way in the fundamental research that has underpinned the development of thin film copper indium diselenide (CIS) based photovoltaics. These devices have demonstrated exceptional energy conversion efficiencies (>19%) and a high tolerance to radiation damage and are thus leading researchers towards the 20% efficiency barrier. Conventional CIS thin film growth processes require a post-selenisation step to incorporate Se into the as-grown material. This helps to achieve stoichometry, improves the crystallinity, controls the defect structure and also can be used to convert the semiconductor type. This paper will report the use of pulsed dc magnetron sputtering from a CIS powder target. This approach has resulted in as–grown stoichiometric thin films consisting of pinhole free, densely packed grains. An important consideration in the thin film growth of complex materials is that stoichiometry is maintained throughout the film. Conventionally, secondary ion mass spectrometry (SIMS) is used to depth profile thin films but it has been reported that laser induced breakdown spectrometry (LIBS) can also be used. We will report the initial results comparing and contrasting these two techniques and show that LIBS can produce meaningful data.

Keywords: LIBS, CIS, depth profiling, SIMS, copper indium diselenide, photovoltaic

1. Introduction

In the early 1970's the Salford photonics group was the first in the world to publish data on CIS [1,2]. We have continued to enjoy several first's in this area which has ultimately led to the development of current world-record CIS solar cells

To date there is still a great performance discrepancy between laboratory produced $CuInSe_2$ / $Cu(In,Ga)Se_2$ (CIS/CIGS) cells and commercially produced modules [3-5] with commercial cells having an efficiency of approximately 12% and laboratory cells regularly nearing 20%. It is the aim of continued research to find simplified processes that will allow the deposition of stoichiometric CIS/CIGS thin films using a single stage process capable of producing large area device quality material.

Sputtering has been repeatedly used for manufacturing CIS/CIGS and related materials. In general there are two approaches: sputtering from a compound target using rf power [6-9] or sputtering from elemental or alloy metal targets followed by a selenisation process (Se-vapour, or H_2Se) [10,11].

The incorporation of a magnetron improves the plasma stability and allows the use of lower process pressures, resulting in decreased scattering of the sputtered particles. Due to increased ion bombardment, the thin films become denser and more uniform. The relatively new technique of Pulsed dc Magnetron Sputtering PDMS has transformed the deposition of insulating materials. Pulsing the supplied dc voltage suppresses destabilising discharges and removes many of the target preparation problems [8,12,13].

2. Pulsed dc Magnetron Sputtering (PDMS)

PDMS is widely recognised as a new technology for the deposition of dielectric materials [12]. The magnetron discharge is pulsed in the mid frequency range 50 – 350 kHz and this alleviates the main problem associated with continuous dc reactive sputtering of such materials, namely arc events at the target. The correct selection of the dc pulse parameters i.e. frequency, duty and reverse voltage, results in extended arc-free operating conditions, even during the deposition of highly insulating materials [14]. The pulsed sputtering technique is now commercially exploited in many applications, including glass coatings with low emissivity, packaging barrier layers, flat panel displays etc. The inherent process stability during depositions results in reduced structural defects, improved film properties and enhanced deposition rates [15].

The application of PDMS for the deposition of complex photovoltaic materials (such as copper indium/gallium diselenide) from a powder target is a new endeavour. There have been a number of studies related to standard dc magnetron sputtering of copper indium/gallium diselenide from elemental sources, but these systems have been complex in their nature and the produced films required post deposition selenisation [10,11].

3. Experimental

A single unbalanced magnetron source, with an approximate target diameter of 180 mm was used. The system is described in detail elsewhere [13]. CIS powder, crushed from polycrystalline ingots [1,17] was separated to a grain size ranging from 0.05 mm to 1 mm and slightly tamped into the target plate to a thickness of around 3 mm. Its composition as determined by EDX analysis showed that it was non-stoichiometric, having a surplus of Copper and Selenium and hence lacking Indium. The average composition was found to be 29% Cu, 17% In and 54% Se with an estimated error of 4%.

The magnetron was driven by an Advanced Energy pulsed dc power supply, that operated to a maximum frequency of 350 kHz with an adjustable duty cycle between 50 to 100%. A target substrate separation of 150 mm was chosen for these initial runs. The pulsing frequency was varied between 100 to 350 kHz, and the duty cycle was between 50 and 80%. Cleaned glass microscope slides were chosen as the substrate.

4. Results and discussion

Using PDMS resulted in a very stable plasma without the occurrence of any arcing. Process conditions such as argon pressure, target-substrate-distance and input power combined with pulsing frequency, duty cycle and the substrate biasing were investigated.

A representative selection of results for films grown under a range of conditions is given below in table I. In general it was found that the final composition remained close to stoichiometric and was largely insensitive to the process parameters.

Table 1. Example deposition conditions including the resulting composition obtained by EDX.

Sample No	Frequency kHz	Bias	Cu %	In %	Se %
1.8	350	n.a.	23.5	24.8	51.7
1.16	170	rf	23.6	23.9	52.5
1.22	130	rf	24.8	24.1	51.1
1.30	170	p. dc	23.5	25.1	51.4
1.35	130	p. dc	24.5	24.9	50.6
1.42	220	rf	24.1	25.1	50.8

It was also noted that the composition of the target powder remained largely unchanged from run to run.

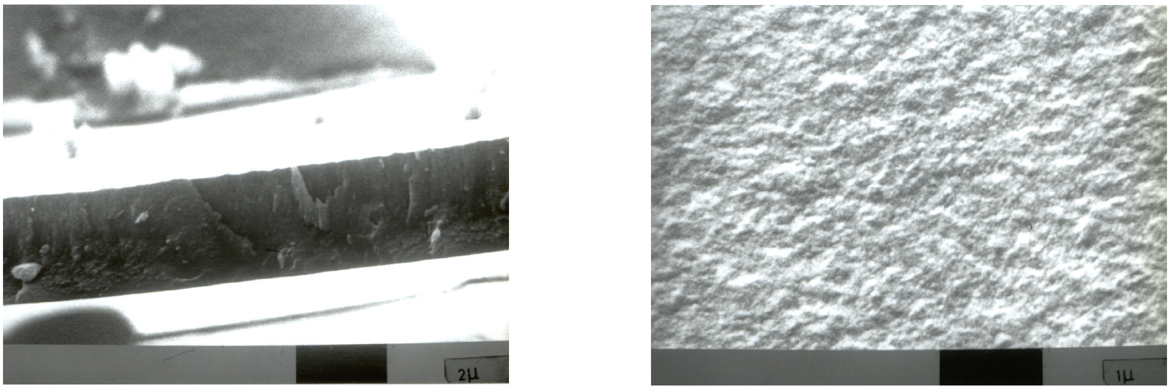


Figure 1 SEM images of as-grown 2 µm thick CIS films

The major result of this study is that stoichiometric CIS thin films could be manufactured from a clearly non-stoichiometric powder target. The reasons for this are unclear, however this may be a feature of CIS when it is dc sputtered from a powder target.
The sputtering yields of Cu, In and Se are quite different from each other and it could be assumed that after an initial period an equilibrium state should be achieved, where the composition of the flux is identical to that of the target material. However, this would not seem to apply here or at least stands in contradiction with the results obtained. Until target powders with different overall compositions have been utilised and analysis of the plasma is undertaken, these conclusions are limited

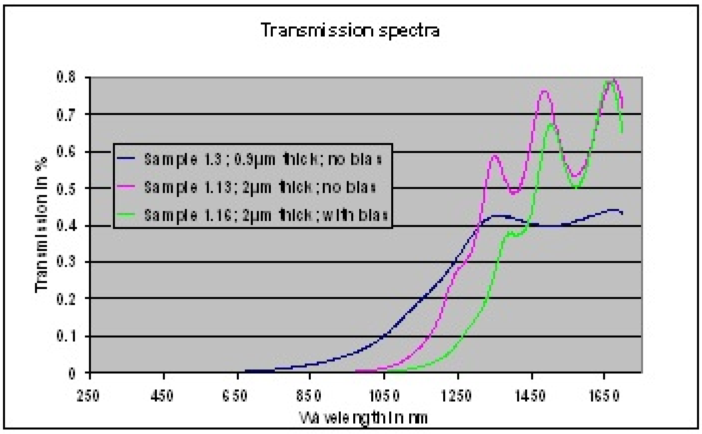


Figure 2
Representative transmission data

Optical measurements revealed that all films had almost 0% transmission in the 300 – 1050 nm range.

4.1. SIMS Profiling

Secondary ion mass spectrometry SIMS, was used to determine compositional changes throughout the thickness of the films. As there are several isotopes of these elements (i.e. ^{63}Cu and ^{65}Cu) their ratios were recorded and compared. The measured and normalised ratios were identical for all films and close to the nominal values.

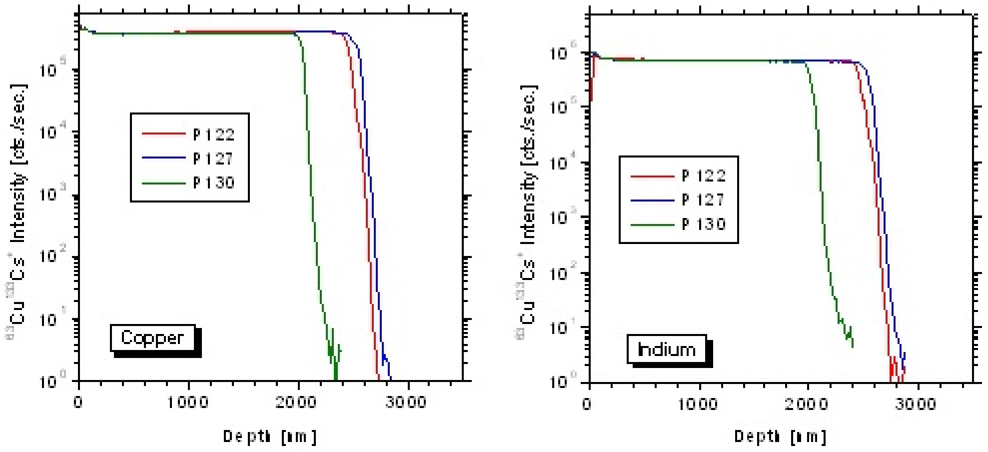
Two major observations were evident from the recorded signals:

I. The compositional relation between the three constituents remained constant through the entire film thickness (Figure 3).

II. The intensity of the ^{80}SeCs$^+$ signal was lower then expected for a corresponding real or nominal stoichiometric composition of CuInSe$_2$ - if compared to the Cu and In signal intensities. Therefore the actual ratio between the signals was the most likely to be incorrect. This is probably due to SIMS artifacts (i.e. instrument memory effects), as has been suggested by Guibertoni and Bersani [18].

The observed signal intensities for Cu, In and Se were at a constant level throughout the entire thin films, indicating compositional uniformity.

The films analysed were deposited with different biasing voltage waveforms (P122: rf; P127: dc; P130: pulsed dc) and the signal intensities of each of these species were compared. Figure 3 illustrates that no relevant variations of composition with thickness could be detected.



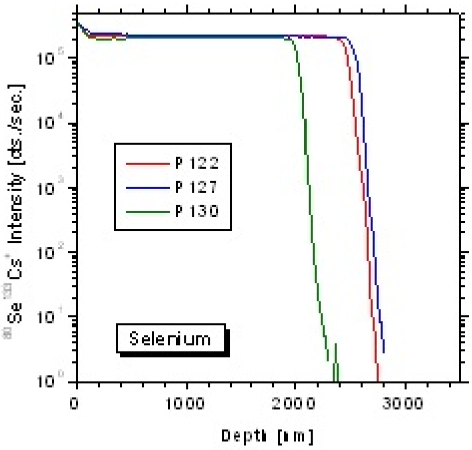


Figure 2 SIMS comparison of copper, indium and selenium depth distributions.

4.2. Laser induced breakdown spectroscopy (LIBS) depth profiling

CIS thin films grown on silicon were ablated using a frequency doubled Nd:YAG laser at a wavelength of 532nm and at fluences between 0.8 Jcm-2 to 0.15 Jcm-2, removing approximately 95nm to 1300nm of material with each shot. Typical depth resolution for LIBS depth profiling is in the range of 100-500nm per shot, but in certain cases average depth per shot values below 10nm have been reported [19,20]. A series of single shot laser pulses was focused at a single point on the sample and selected spectral emission lines relating to the elements present in the films and substrate were recorded; Si: 390.55nm; In: 451.13nm; Cu: 521.82nm. The beam profile of this laser is pseudo Gaussian (not 'top hat') and as a result it is not possible to produce a clear cut off between substrate and deposited material.

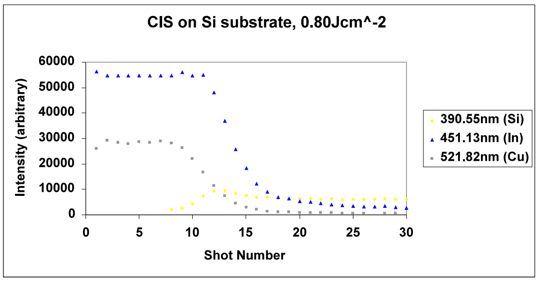


Figure 4 LIBS profiles

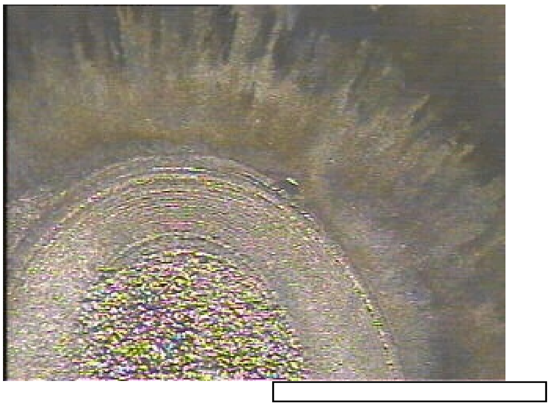


Figure 5 The ablated CIS region

The LIBS spectra support the SIMS data, again showing that the composition of the CIS films is uniform throughout. This photographic image of ablated CIS on a Si substrate clearly shows the exposed silicon substrate in the centre of the ablated region, together with evidence of re-deposition.

5. Conclusions

The work described has shown that dc magnetron sputtering can produced close packed stoichiometric thin films of copper indium diselenide without the need for a post deposition selenisation step and using simple powdered targets with a non-stoichiometric composition. The optical transmission characteristics of the films indicate an unusually high degree of absorption at visible wavelengths. Conventional SIMS analysis showed the films to be of uniform composition throughout their thickness and this result was confirmed by laser induced breakdown spectroscopy measurements, suggesting that this technique could offer a useful additional method for compositional analysis.

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