Towards deposition of copper indium gallium sulphide/selenide materials by chemical vapour deposition

Daniel W. Hewak, Kenton Knight, and Kevin C. C. Huang
Optoelectronics Research Centre, University of Southampton, Southampton, SO17 1BJ, United Kingdom

ABSTRACT
Copper indium gallium sulphide thin films have been fabricated by chemical vapour deposition with metal halide precursors and S_2Cl_2 and H_2 reactive gases. The CVD-grown CIGS thin films have been characterized by scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffraction analysis, and UV-VIS-NIR spectroscopy.

INTRODUCTION
Chemical vapour deposition (CVD) is a widely used method in the optoelectronics and semiconductor industries to produce high purity thin films. The advantages of CVD processing, which offers offer superior quality compared to conventional methods such as sputtering or co-evaporation, include conformality, coverage, and stoichiometry control.
Since 2001, we have been developing new CVD technology for the chalcogenides and are now routinely depositing germanium and antimony based sulphides on a variety of substrates [1]. Copper indium gallium sulphide/selenide (CIGS) is an important chalcogenide material which is typically deposited by vacuum-based processes which co-evaporate or co-sputter copper, gallium, and indium, after which the resulting film is annealed with a sulphide/selenide vapour to form the final CIGS structure [2]. A non-vacuum-based alternative process deposits nanoparticles of the precursor materials on a substrate and then sinters them in situ [3].
We report here on efforts to extend our CVD technology to the CIGS family of materials and in doing so improving material quality and process repeatability. Our work focuses on the use metal halide precursors such as CuCl, $GaCl_3$, $InCl_3$ which are reacted in situation with processing gases such as H_2 and S_2Cl_2.

APPARATUS
The CVD apparatus we have constructed for CIGS thin film deposition is shown in figure 1. In the process we exploit, CIGS thin films were deposited on microscope slide substrates placed in the quartz tube reactor and heated by a special designed three-zone electrical resistance furnace to provide a gradient temperature distribution inside the furnace. The precursors, GaCl3, InCl3, and CuCl were placed between two silica wool buns inside individual quartz tubes. These precursors were liquid inside the furnace and were vaporized with argon gas through the mass flow controllers (MFC) at a flow rate in the range of 50 ml/min-150 ml/min. The reactive gases, 6%H_2 balanced in argon and S_2Cl_2 vapour delivered by argon gas , were both controlled by MFCs at the flow rate of 350ml/min and 250ml/min respectively.

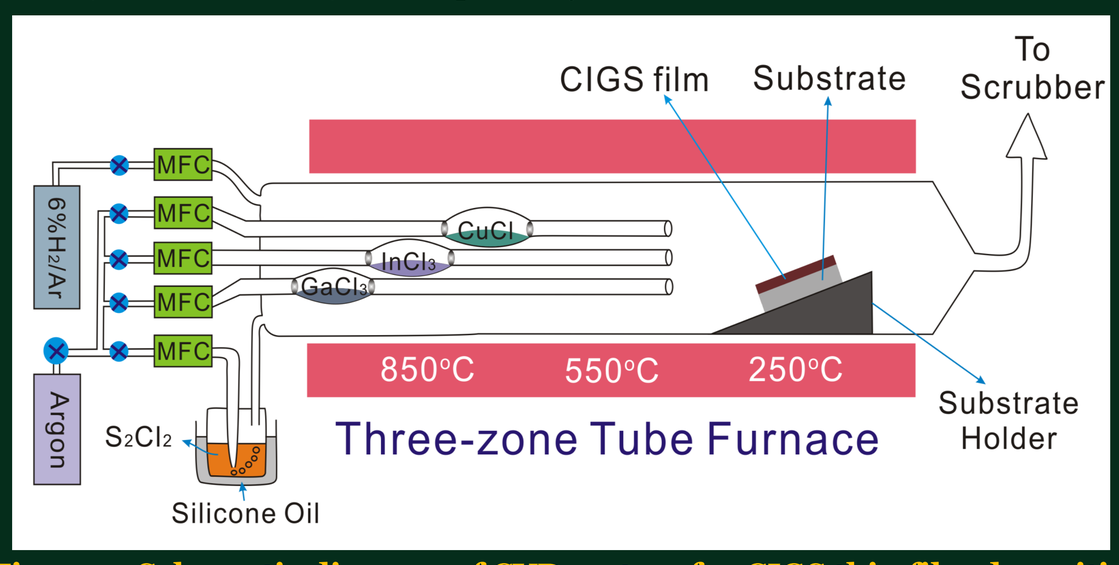

Figure 1: Schematic diagram of CVD system for CIGS thin film deposition.

RESULTS AND DISCUSSION
CIGS thin films were deposited on microscope glass slides and then characterized with a scanning electron microscope (SEM) (Fig. 2a). The composition of these films was determined by energy dispersive X-ray (EDX) analysis and the result of the CIGS film shown in Fig. 2a revealed that $Cu_{11}In_{26}Ga_8S_{55}$ have been achieved by our CVD method . The thickness of CIGS film was also determined by SEM micrographs (Fig. 2b) of the edge profile of a cleaved sample. From Fig.2b, the CIGS film with the thickness of about 36 µm has been achieved in 2 hours deposition and therefore the deposition rate is approximately 0.3 µm/min.

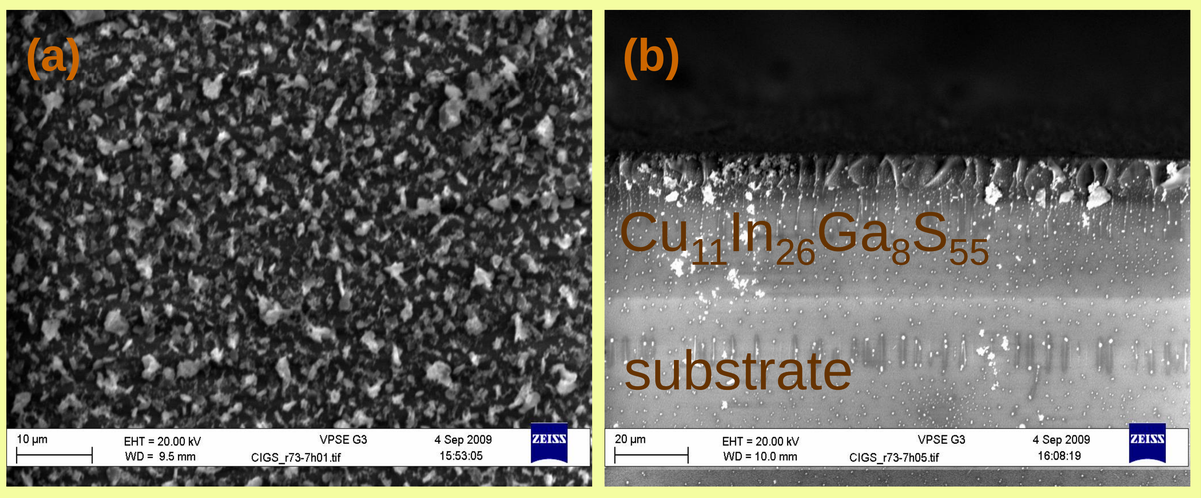

Figure 2: Typical SEM micrograph of the top view (a) and cross section (b) of a CIGS film deposited on a microscope slide substrate .

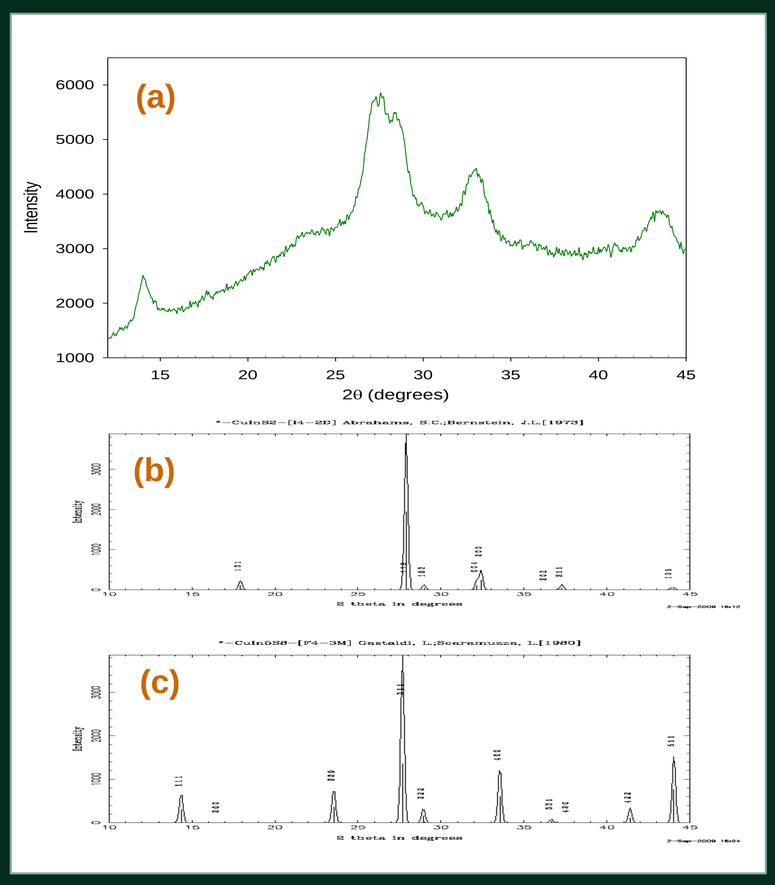

Figure 3: XRD patterns of CVD grown $Cu_{11}In_{26}Ga_8S_{55}$ film (3a), XRD patterns of $CuInS_2$ from data base (3b), and XRD patterns of $CuIn_5S_8$ from data base (3c).

From the X-ray diffraction (XRD) patterns of the CVD-grown CIGS film (Fig. 3a), two crystalline phases, Cu(In,Ga)S_2 (Fig. 3b) and Cu(In,Ga)$_5S_8$ (Fig. 3c) have been found in this $Cu_{11}In_{26}Ga_8S_{55}$ composition. Moreover, the background in Fig. 3a is relatively high which indicates that the amorphous phase co-exists in the CVD-grown CIGS film, which is likely as the substrate temperature was kept at 250°C. However, control could be improved by increasing the substrate temperature and changing the flow parameters.

The transmission spectrum of this CVD-grown $Cu_{11}In_{26}Ga_8S_{55}$ film was measured by a Varian Cary 500 UV-VIS-NIR spectrometer shown in Fig. 4 . The result reveals that the band gap of this 36 µm thick CIGS film is about 0.9 eV.

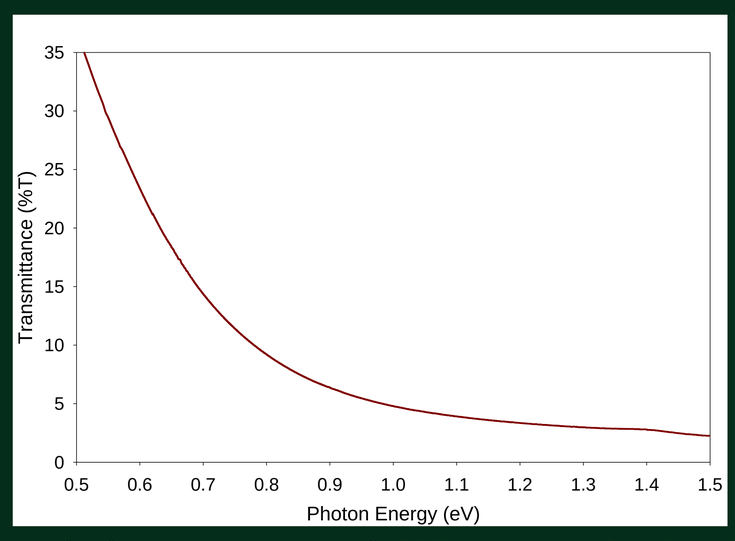

Figure 4: Transmission spectrum of CVD grown $Cu_{11}In_{26}Ga_8S_{55}$ film on microscope glass slide.

CONCLUSION
$Cu_{11}In_{26}Ga_8S_{55}$ films have been successfully fabricated by CVD technique. The composition and surface morphology of these films have also been characterized by SEM and EDX techniques. XRD patterns of the CVD-grown CIGS film reveal two crystalline phases , Cu(In,Ga)S_2 and Cu(In,Ga)$_5S_8$ have been formed. The band gap of this CVD-grown CIGS film is about 0.9 eV from the transmission spectrum. The preliminary results of fabrication of CIGS films by CVD with metal halide precursors are very promising. We are now working on the improvement of film quality and adding Se into CIGS films by our CVD techniques.

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ACKNOWLEDGEMENTS
The authors would like to acknowledge the technical assistance of Mr. John Tucknott, Mr. Neil Fagan, Mr. Mark Lessey and Mr. Trevor Austin. This work was funded by the Engineering Physical Sciences Research Council through our Portfolio Grant EP/C515668/1.