

The Discovery and Optimisation of Solid State Materials for the Energy and Electronic Sectors using MBE Based Methodologies

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ABSTRACT

Compositional gradient thin film materials prepared by simultaneously combining the atomic constituents through the use of Knudsen cells, cracking sources, e-beam sources or plasma atom sources provide a powerful route to materials discovery and optimisation. A kinetically favourable route to solid state crystalline materials is provided, often through the synthesis of the metastable nano-crystalline or amorphous phases. A consequence is that complex materials can be produced at lower crystallisation temperatures, and that high quality, dense thin films are produced. The addition of “wedge” shutters allows excellent control of composition space over areas suitable for screening on micro-fabricated MEMS arrays. A wide range of elements can be incorporated in the materials which are of high purity as a result of the UHV environment for synthesis. The method is also suitable for producing combinatorial ranges of supported nano-particles in the size range (1-10nm) where strong size dependent catalytic activity is observed. These important advantages are exemplified here in the synthesis of a range of platinum particle sizes on carbon which have been subsequently screened for oxygen reduction activity in an environment appropriate to mimicking the cathode of a low temperature PEM fuel cell. A second example is provided in the comparative direct and indirect synthesis of CIGS materials, and their primary screening for potential thin film photovoltaic applications

Keywords: high-throughput, thin-film, materials, nano-particles, catalysis.

1 INTRODUCTION

There have been considerable developments in the combinatorial or high-throughput discovery of materials over the last 15 years, largely as a result of synthesis method development, high sensitivity characterisation, and effective screening of function on thin film materials grown with the compositional gradient approach. The demands of the synthetic methodology have increased as the materials classes have extended from multicomponent polycrystalline metal alloys to amorphous and crystalline oxides, nitrides and chalcogenides, supported nano-particles and metal hydrides. This challenge results from the demands in an

increasing range of material function particularly in the energy and electronics sectors. Combined with appropriate screening methods one can find examples of the discovery and optimisation of, for example, dielectric, tunable dielectric, ferroelectric, piezoelectric, phase change, hydrogen storage, lithium ion battery and fuel cell electrocatalyst and photocatalytic materials. There are advantages of each of the various thin film methods (mainly sputtering and PLD) used for the synthesis of the various classes of solid state materials in a form and format appropriate for screening. However, an important adaptation of the method that allows successful combinatorial synthesis is the intimate mixing of the constituent components in the thin film. This is required in order to minimise activation barriers associated with bond breaking and diffusion during the formation of the target material, a problem familiar to the bulk solid state synthetic community who rely on nano-particle formation and mixing using techniques such as grinding or ball milling, sol-gel, or hydrothermal chemistries.

Thin film synthesis of compositional gradient thin films from atomic MBE sources, cracker sources and plasma atom sources[1] inherently overcome the kinetic barriers of mixing through the simultaneous deposition of the atoms randomly in the film during growth. When carried on a 300K substrate, the result is often an amorphous or microcrystalline material in a metastable state. A relatively low energy (temperature) is subsequently required for the formation of the ground state. This is particularly important in the formation of relatively volatile materials, and particularly with solid state materials containing molecular ions. The MBE based methods also allow access to a wide variety of component elements, including lithium, sulphur and phosphorous. The introduction of wedge shutters on the sources allows the simultaneous deposition of the atomic components while allowing excellent control of the compositional gradient in an area compatible with cost effective MEMS array screening chip formats. This approach has been pioneered in the commercial sector by Ilika technologies, and it has been successfully applied to a number of the functional materials sectors highlighted above.

Described briefly here are two contrasting systems where the method has been used to highlight its flexibility in the synthesis and screening of supported nano-particles as catalysts (specifically fuel cell cathode catalysts), and in

the direct synthesis of dense sulphide thin films (active layers in thin film photovoltaics).

2 SULPHIDES

Thin film photovoltaics based on chalcogenide based absorber materials such as $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (CIGS) can offer comparable conversion efficiencies to silicon based cells when successfully synthesised in composite layers with compatible buffer and TCO layers. The challenge remains optimising the material selection in the layers, and their reliable synthesis. The development of a high throughput synthetic and screening methodology would accelerate the optimisation of such systems. Reported here is a direct synthetic route to complex sulphide thin films of high quality, a route contrasted with a sequential synthetic approach which fails to achieve single phase, high quality thin film materials which will be required for materials selection and optimisation. The $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ solid solution phase was chosen to benchmark the methodology [2] as the materials are well reported in the literature.

2.1 Two Step Synthesis

The two-step method involved evaporation of CuInGa thin film precursors onto various substrates by elemental evaporation from Knudsen effusion cells or electron beam sources and a subsequent sulphurisation of 30 minutes in a flow of H_2S in Ar at 450°C . Figure 1 shows the compositional range and sulphur stoichiometry for such a CuInGaS library in the region of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ solid solution phase measured by EDS (100 points). Within experimental error the expected sulphur stoichiometry was obtained. Each site on a single thin film of CuInGaS exhibited the desired sulphur stoichiometry ($50 \pm 5\% \text{At}$), although an apparent excess of sulphur appears in the Ga-rich region. Figure 2 shows the change in appearance of the film before and after the sulphurisation step.

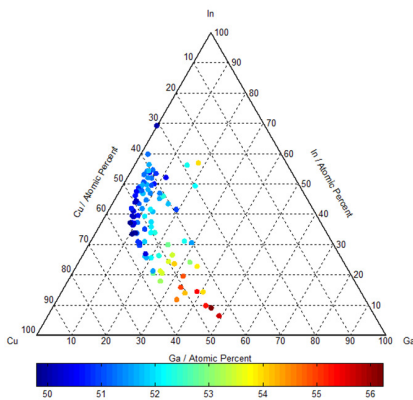


Figure 1: The compositional range (100 analytical points from EDS) of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ thin film (two step synthesis) showing the range of sulphur stoichiometries (colour bar represents $\text{S } \%_{\text{At}}$).

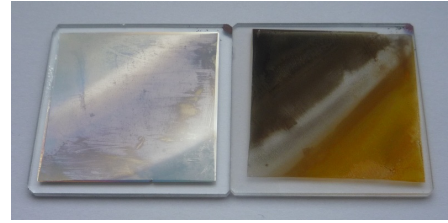


Figure 2: Images of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ thin film (two step synthesis) before and after sulphurisation.

There has clearly been a deterioration of the thin film material, particularly across the centre of the sample corresponding to the compositional region around $x=0.5$. X-ray diffraction measurements carried out on the thin film library shows the chalcopyrite structure has been formed with the $\langle 112 \rangle$ at $2\theta = 27-29^\circ$ and $(220/204)$ at $2\theta = 46-48^\circ$ planes dominating the diffraction patterns, the shifts in the peaks associated with the substitution of Ga and In in the lattice. If $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ behaved as a purely solid solution, the shift in 2θ would be linear [3] obeying Vegard's Law. However for intermediate In:Ga ratios (x around 0.5), a doublet is observed in the $\langle 112 \rangle$ Bragg peak (Figure 3). A plot of the peak shift for $\langle 112 \rangle$, also shown in Figure 3, emphasises what is happening in the library: at the high In or Ga concentrations, substitution in the lattice takes place as in a solid solution, but for the intermediate composition region a strong deviation is observed and two separate phases are formed (an apparent immiscibility gap). This problem of accessing the complete solid solution range derives from the two step synthesis, since the In and Ga can phase segregate prior to complete sulphurisation.

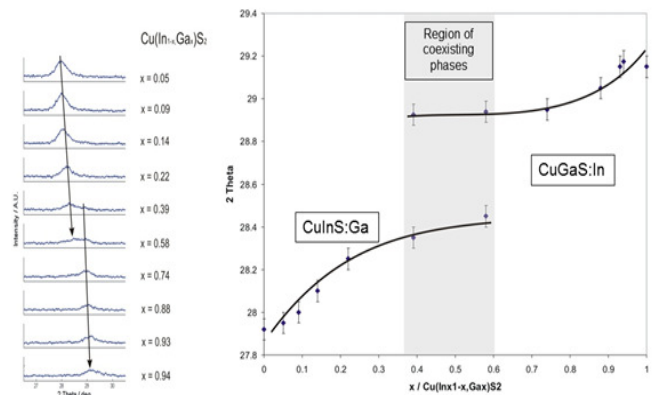


Figure 3: The peak shift of the $\langle 112 \rangle$ Bragg reflection of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ tetragonal chalcopyrite thin film (two step synthesis) as a function of the Ga to In ratio.

2.2 One Step Synthesis

Samples were also synthesised using a one-step deposition method. Cu, In, Ga and S were simultaneously evaporated by effusion cell or e-beam source to produce the

compositional gradient library. The sulphur effusion source comprises a modified K-Cell with a molybdenum cracker insert on the source lip, held at a higher temperature than the effusion zone, to crack the evaporated sulphur molecules to atoms. Figure 4 shows the compositional range and sulphur stoichiometry for such a CuInGaS library in the region of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ solid solution phase measured by EDS (100 points), indicating a narrow range (within experimental error) of the expected sulphur stoichiometry of $50 \pm 2 \text{ \% At.}$

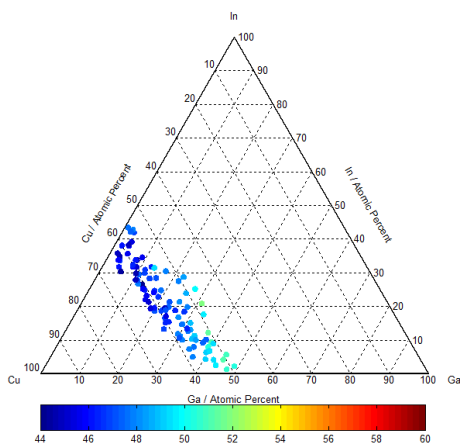


Figure 4: The compositional range (100 analytical points from EDS) of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ thin film (one step synthesis) showing the range of sulphur stoichiometries.

An optical picture of the sample is shown in Figure 5, indicating a homogeneous thin film of material across the sample (in contrast to that obtained in the two step synthesis in Figure 2).

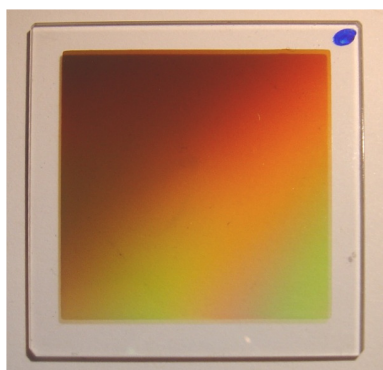


Figure 5: Images of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ thin film (one step synthesis) before and after sulphurisation.

The corresponding XRD shows the formation of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ tetragonal chalcopyrite phases in the solid solution composition range, and a linear compositional dependence of the associated $\langle 112 \rangle$ Bragg peak (Figure 6) shows a linear dependence of the peak position as one would expect [3] for a complete solid solution over the complete compositional range.

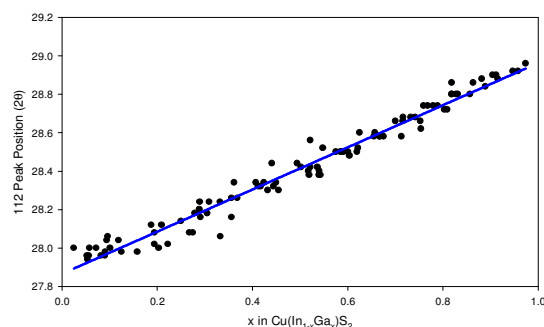


Figure 6: The peak shift of the $\langle 112 \rangle$ Bragg reflection of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ tetragonal chalcopyrite thin film (two step synthesis) as a function of the Ga to In ratio.

2.3 Conclusions

For a one-step synthesis of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ tetragonal chalcopyrite thin film in a compositional gradient by simultaneous combination of the elements from atomic MBE sources, a homogeneous thin film can be directly formed across the complete solid solution range. In contrast, phase segregated materials are produced in a two stage (indirect) process. Not only can crystalline materials be synthesised directly, but amorphous materials are also accessible at lower substrate temperatures.

3 SUPPORTED NANO-PARTICLES

MBE based methods have also been used to form libraries where the particle size (in the range of 1-10nm diameter) of metals can be controlled and varied (through nucleation and growth) across a supporting material. [4] The method has been used to demonstrate the importance of particle size and oxide support composition and morphology in electrocatalysis relating to low temperature fuel cell electrode optimisation. Results presented here [5] briefly show the synthesis of such a Pt particle library on carbon, and its screening for oxygen reduction activity. It is demonstrated that the predictions of the optimal electrocatalyst in the high throughput thin film library are consistent with observations of the high area carbon supported Pt catalysts used in PEM fuel cells [6].

3.1 Pt Particle Synthesis on Carbon

Carbon was deposited from an e-gun on a number of substrates including 10×10 electrochemical screening arrays [7] and a corresponding array of TEM grids. Low and varying effective thicknesses of Pt were subsequently deposited across the arrays (at 350K) using the wedge shutter, and particles of Pt of varying size were nucleated. Figure 7 shows a series of TEM measurements formed on the grids at 4 points across the array, and the average particle size indicated.

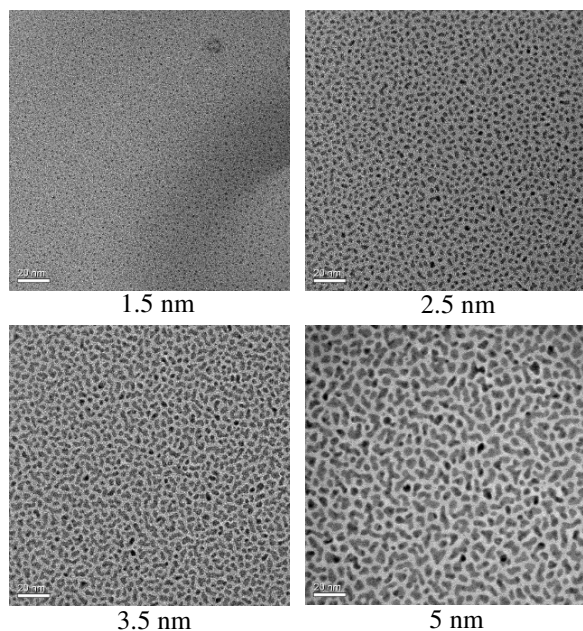


Figure 7: Nucleation and growth of Pt particles on carbon at 4 points across the library measured in TEM.

From these 4 calibration points, because of the linearity of the wedge deposition control, the Pt particle size at every point across the electrochemical array could be predicted (Figure 8).

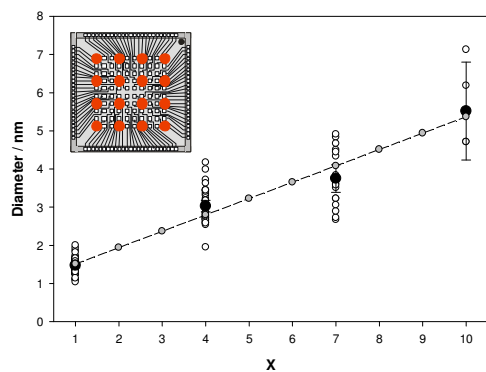


Figure 8: Calibration curve used to deduce Pt particle size across an electrochemical screening array (inset).

3.2 Pt on Carbon: Catalyst Activity

Figure 9 shows the results of screening the carbon supported Pt particle library simultaneously [6, 7] for its oxygen reduction activity. This is the rate limiting (cathode) reaction of low temperature PEM fuel cells. The mass activity of the platinum catalysts is calculated (from the measured specific activity) and plotted in Figure 9 as a function of Pt particle size. Measurements have been averaged across each row of 10 electrodes which correspond to the same particle size. The results reveal an optimum in the platinum particle size for this reaction around 3.8 nm.

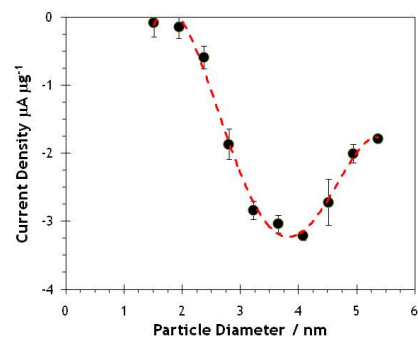


Figure 9: Particle size dependence of oxygen reduction reaction current density.

3.4 Conclusion

These results clearly show the ability of the MBE high throughput methodology to control particle size in a library. It also shows the importance of particle size in optimising a catalyst performance. Indeed these results correspond well with those found on high area supported commercial catalysts [6]. The method can be extended to produce alloy particles of varying composition, and by combining with compositional gradients of support materials, complex catalyst systems become accessible for discovery and optimisation.

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