

Use of combinatorial analysis for the study of new material for solar cells applications

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Abstract

This paper presents a combinatorial method for the deposition and characterization of new metallic precursors for photovoltaic materials. One-dimensional thin film alloy "libraries" were electrodeposited on Mo-coated glass. The library elements were deposited in two consecutive baths and then heated in a reducing atmosphere to promote inter-diffusion of the elements. At the end of this process, the libraries possessed a composition gradient along their lengths, with single elements at their two opposite ends and one or more alloys and/or a solid state solution in between. This continuous range of compositions can therefore be considered a collection of specific precursors that can be interrogated by examining their corresponding locations, with the crystallographic structure along the library changing in accordance with the phase diagram for the metals.

The libraries were then sulphurised or selenised by heating in a sulphur-rich or selenium rich atmosphere; this converted the metallic precursors in a continuous range of materials, candidates for potential solar cells absorbers. The libraries were analysed by X-ray diffraction and energy dispersive X-ray spectrometry. The X-ray diffraction results show phase changes across the libraries, which can be correlated with the original precursor concentration at that particular point.

Introduction

The development of materials for solar cells applications has evolved from those with a single element structure, such as Silicon, to more complicated compounds such as Cu(In,Ga)Se₂. This evolution has been motivated in an attempt to reduce

production cost and improve the chemical and physical properties of the as-deposited films which lead to the fabrication of devices with an excellent light-to-current conversion levels. However, abundance and toxicology issues allied with high-cost purification processes for some materials have limited the large scale commercialisation of these products. As a result, research is now focussing on new polycrystalline materials for solar cells applications.

Sulphide materials can have semiconductor properties useful for solar cells application [1,2]. Copper and bismuth are attractive alternatives as absorbing layers in photovoltaic devices due to the absence of toxic elements and their abundance. Development of these Cu-Bi-S compounds as well as other possible solar cell precursor materials can potentially be aided by the employment of combinatorial production and analysis methods which have been shown to be successful in a number of material science applications [3]. While high density chemical libraries with discreet and highly defined areas are useful, particularly, in late stages of development, for initial assessments it is more prudent to concentrate on continuous compositional spread samples with large and fast changing compositional gradients. A three step method was followed to deposit the Cu-Bi-S and Cu-Bi-Se libraries (as described below) involving the deposition of the two metals precursor layers followed by a heat treatment in a reactive atmosphere (sulphur or selenium gasses in this case).

Experimental

The preparation of the thin film libraries utilises two popular deposition methods. Initially direct current (DC) magnetron sputtering was used to deposit a uniform layer of molybdenum ~860nm onto soda lime silicate glass, this acted as a conducting layer for the electrochemical steps, and in device structures would form the back contact.

Copper was deposited using an alkali electrochemical bath with the following composition: NaOH 2M, Sorbitol 0.1 M and CuCl₂ 0.1M. The applied potential was -1.1 V as this has been found to produce efficient deposition with this bath. Initially the sample was positioned so that 1mm of unmasked substrate was submerged in the bath and was therefore available for deposition. During the deposition the level of electrolytic solution was raised at a rate of ~2 mm min⁻¹ so that the time allowed for deposition ranged from 30 minutes to 20 seconds across the sample. In this way a film with thickness ranging from 2µm to 50nm was produced.

The substrate was then inverted and positioned in a bath of composition, NaOH 2M, Sorbitol 0.2M, Bi(NO₃)₃ 0.05M, with an applied potential of -0.83 V. The deposition time ranged from 20 minutes to 15 seconds at the extreme ends produced a complementary layer of Bismuth and therefore the required continuous compositional spread (CCS) sample. The masked edges of the sample remain solely the sputter coated molybdenum.

Each sample was pre-treated at 200 °C for 3 hours in 10 % H₂ / N₂ at atmospheric pressure. Sulphurisation was then carried out by the addition of 0.3 g of solid sulphur (x100 excess to that required for complete conversion) in flowing atmospheric pressure N₂. Temperature ramped at 5 °C min⁻¹ to 450 °C then held for 30 minutes before cooling. These comparatively mild conditions reduced the likelihood of film de-adhesion, caused by a more rapid addition of sulphur.

For selenisation elemental Se was thermally evaporated onto the samples' surfaces, they were heated at either 250 or 450 °C under excess Se, then held for 1 hour under a 20 mbar 10 % H₂ / N₂ atmosphere.

X-ray diffraction (XRD) data were collected in reflection using a Bruker D8 diffractometer fitted with a GADDS detector. The incident X-ray beam (CuKα)

was conditioned to produce a beam of ~1 mm x 1 mm at the sample using a single Geöbel mirror. Scattering data were corrected for detector distortions (geometric & response) prior to analysis.

Energy dispersive X-ray analysis was completed using a LEO 435VP SEM, EDAX system and Genesis software. An accelerating voltage of 15 kV was used for all positions.

In all cases the measurement were taken by line scanning across the full substrate so that the edges can be used to accurately fix each points co-ordinates. The step size between points was 2 mm in all cases, see Figure 1.



Figure 1 Sample measurement point location.

Results and Discussion

The copper-bismuth equilibrium diagram shows a eutectic point at 99.5% bismuth and 270.6°C. At room temperature, a solid state solution is formed due to the complete miscibility of the two metals.

The XRD contour map of the as-deposited Cu-Bi library is shown in Figure 2. The main peaks have been identified and assigned to the two precursor metals (Cu and Bi). An intense peak can be observed in the centre of the graph which has been identified as the Mo substrate. The first ~1 cm at each edge of the samples are not coated with the Cu-Bi layer hence Cu and Bi peaks are absent from these regions and the Mo peak is particularly strong. A small area of the sample was covered only by Bi which is observed between 10 and 20 mm on the contour map the same is the case for copper pure copper which is detected between 47 and 52 mm. In the central region of the library, a mixture of the two metals is observed. These observations are confirmed using EDX analysis (Figure 3) which shows a variation of the relative concentrations of the two metals from one edge of the library to the other. The XRD results show no alloys are formed as no shift is observed in the peak positions for copper and bismuth which is generally an indicator of a solid state solution being formed.

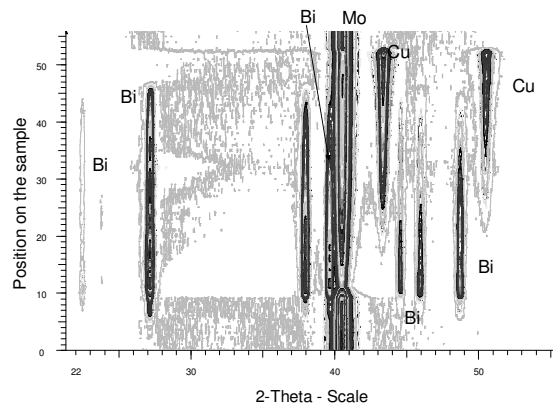


Figure 2: Contour Map of the Cu-Bi Untreated Library (position in mm).

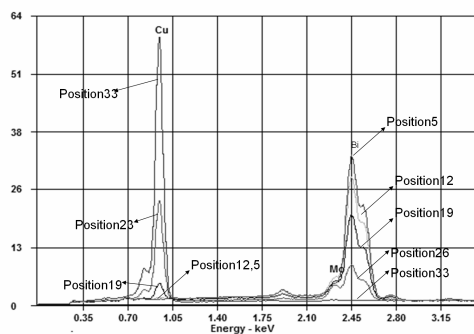


Figure 3: EDX Analysis of the Cu-Bi untreated Library

The heat treatment performed at 200 °C did not promote the inter-diffusion of the two elements as observed by comparing the un-treated (Figure 2) and the heat treated XRD contour maps (). This temperature was selected to be below the bismuth melting point as at higher temperatures the treatment runs the risk that the bismuth in the sample would be lost causing degradation of the library.

Previous studies on the formation of Cu_3BiS_3 show different conversion velocities between CuS and Cu_2S . The conversion of CuS and Bi is completed in 1 hour at 300 °C [4], while the conversion of Cu_2S and Bi at 270 °C is observed only after 30 hours treatment [5]. This suggests that the heat treatment process performed on the samples in our study needs to be extended over a longer period in order to successfully achieve inter-diffusion.

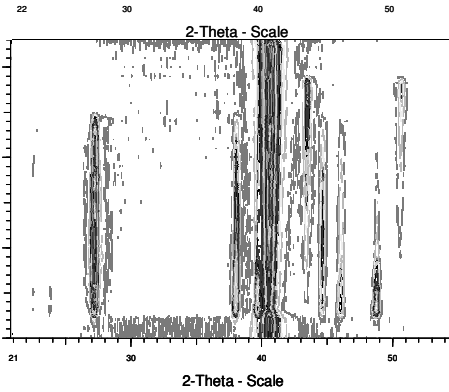


Figure 4: Contour map of the heat treated library. Position in mm.

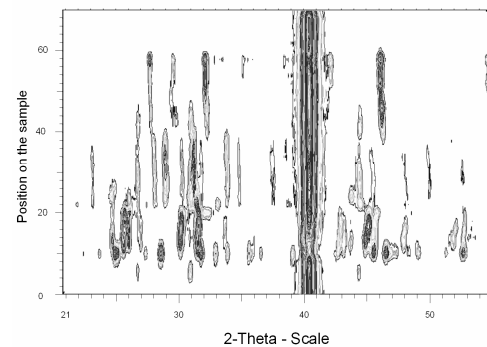


Figure 5: Contour map of the sulphurised library. Position in mm.

Sulphurisation and selenisation treatments were performed on the heat treated libraries. The sulphurisation process produced a number of extra phases which are very difficult to identify due to a lack of information about the ternary-alloys diffraction pattern. However an analysis of the patterns (Figure 5) did indicate that,

- Points 1 to 4 are the uncoated Mo layer.
- The XRD diffractogram peaks of the first few measurement positions (from points 5 to 8) corresponded to the Bi_2S_3 phase which is formed due to the reaction of Bi with sulphur gas.
- The positions from points 9 to 12 correspond to $\text{Bi}_{4.8}\text{Cu}_{2.94}\text{S}_9$ which it is thought to be formed by a reaction between Cu and Bi and the sulphur gas.
- Positions 13 and 14 remain unidentified, while positions 15 to 25 have been assigned to Cu_3BiS_3 .
- The last part of the library (points 26 to 32) corresponds to the conversion of the copper into Cu_9S_5 .
- The final points, from points 33 to 37 are also the uncoated Mo layer.

The comparison between the untreated Cu-Bi and the sulphurised material in the

EDX results suggest that the Bi may have been lost during the treatment. This is in agreement with other studies which heat treat bismuth [5].

The two temperature conditions were tested in regard to the selenisation of the libraries, this is part of a wider study into temperature dependant phase formation. This aim is to find temperatures that will allow the formation of large numbers of Cu-Bi-Se phases on a single library as this will best exploit the chosen combinatorial production method.

In the case of the low temperature selenisation the library is dominated by a small number of phases that are present over a significant compositional range, albeit often with other minor phases that are also detected by XRD. The first few points of the library (from 33 to 26) the major phase has been identified as CuSe_2 with the other end (below point 15) being dominated by Bi_2Se_3 . The central part of the sample has both of these two phases present in varying concentration, as well as small amounts of copper (such as point. 25). This is expected as the EDX results show a significant change of Cu/Bi ratio in this range.

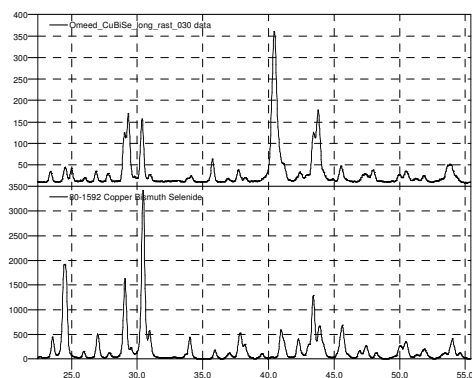


Figure 6 Diffractogram from point 8 of high temperature selenised sample. Top trace experimental data, bottom trace simulation for $\text{Cu}_8\text{Bi}_{24}\text{Se}_{40}$.

High temperature treatment produces significant numbers of phases including material that exists only in a narrow compositional range, a number of these phases remain as yet unidentified due to the paucity of relevant diffraction data but are expected to be $\text{Cu}_x\text{Bi}_x\text{Se}_x$ ternary alloys. Points 30-34 show Cu_2Se , this is joined after point 29 by another unknown phase. Point 8 has been identified as $\text{Cu}_8\text{Bi}_{24}\text{Se}_{40}$ (see Figure 5) this transitions quickly to CuBi and Bi_2Se_3 by point 6.

While the continued reduction in copper concentration means that Bi_2Se_3 in the only significant phase by point 4.

Conclusion

An electrochemistry technique was used to deposit Cu-Bi libraries which then were annealed in a reactive atmosphere to allow the conversion of the metallic layers. Whilst the temperature/time regimes used failed to produce complete interdiffusion, evidence of partial diffusion and conversion to the sulphide or selenide was observed, such as the production of $\text{Cu}_8\text{Bi}_{24}\text{Se}_{40}$. Due the complexity of the samples, future analyses need to be performed to better understand the composition of the libraries and the conversion process, such as RBS measurements to investigate the interdiffusion/alloying process.

Further studies will also be performed to investigate the photovoltaic properties of the libraries to identify suitable stoichiometries for solar cells applications. This could be facilitated using ellipsometry to explore the optical properties of the converted layers. EQE measures using a liquid contact could prove beneficial in accommodating the rough surfaces found on these samples.

Acknowledgements

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References

- [1] V. B. Deshpande, A. P. Sapre, C. Mande, *J Phys C Solid State* 16 (13) (1983)
- [2] L. Gurinovich, V. Gurin, V. Ivanov, I. Bodnar, A. Molochko, N. Solovej, *Phys Status Solidi B* 208 (2) (1998) .
- [3] J. D. Perkins, J. A. del Cueto, J. L. Alleman, C. Warmsingh, B. M. Keyes, L. M. Gedvilas, P. A. Parilla, B. To, D. W. Readey and D. S. Ginley *Thin Solid Films*, 411 (152-160) (2002),
- [4] V. Estrella, M.T.S Nair and P.K. Nair, *Semiconductor Science and Technology*, 18 (190-194) (2003)
- [5] N.J. Gerein and J. Haber, *Photovoltaic Specialists Conference*, 2005. *Conference Record of the Thirty-first IEEE*, 159