High Throughput Synthesis and Screening of Chalcogenide Materials for Data Storage

Robert E Simpson, D W Hewak, Samuel Guerin, Brian Hayden and Graeme Purdy

Optoelectronics Research Centre and School of Chemistry, University of Southampton, Southampton SO17 1BJ
Ilika Technologies Ltd, Centre for Enterprise and Innovation, University of Southampton, Southampton, SO17 1BJ

ABSTRACT

The ability to store information through the phase change mechanism is a well established technology for optical data storage, with typically germanium antimony telluride based films forming the active layer of a phase change disc. However, the ever increasing need for greater storage densities, shorter write/erase duration and longer archival time is driving interest beyond these established materials. Over the past fifteen years, the Optoelectronics Research Centre at the University of Southampton has extensively studied a wide range of chalcogenide glasses, for applications as bulk optical materials, optical fibres and thin film devices. Recently, in partnership with the School of Chemistry and Ilika Technologies Ltd, they embarked on a programme of materials discovery utilizing new high throughput techniques for material deposition and characterization, with the objective of identifying new and improved materials for the phase change memory market.

1. INTRODUCTION

This work introduces a method of high throughput combinatorial deposition and screening of chalcogenide based alloys for both optical and electrical phase change data storage. Combinatorial methods are commonly applied to pharmaceutical drug discovery and more recently these high throughput methods have been applied to other areas of chemistry and materials science. The controlled synthesis of a large number of different material compositions under identical conditions is clearly an attractive prospect in the search for new active and robust materials for any application. This is achieved when the synthesis method is combined with an increasing number of high throughput characterisation methods and measurements of relevant figures of merit [1].

High throughput methods were first applied to chalcogenide compositions by Kyrsta and Cremer *et al* in 2003 [2-3]. Germanium, antimony and tellurium were co-sputtered onto a SiO_2 on Si substrate such that a gradient of the respective elements was achieved across the substrate. These experiments were limited to relatively small compositional ranges around the well characterised $Ge_2Sb_2Te_5$ eutectic composition. The experiment demonstrated the efficiency of high throughput techniques to catalogue the write/erase time and crystal structure dependence on composition. More recently Ramberg *et al* [4] reported further combinatorial phase change experimentation. Their deposition system employed a shutter system to periodically deposit thin films of various elements to create a layered structure. The entire film was then thermally annealed to allow the constituent atoms to mix.

It seems clear that chalcogenide-based phase change materials lend themselves to compositional spread analysis. There are many properties which should be optimised in order to synthesise a useful phase change material while at the same time significant changes in performance can be observed with small compositional variations. The key performance requirements include write/erase times, cycle endurance, minimal cross talk between bits and archival life times. In addition, for optical data storage a good optical contrast is necessary between the glass and crystalline phases. The energy efficiency of the system is also affected by the films ability to absorb a large proportion of the optical energy incident upon it; thus implying further restrictions on the films properties. For the next generation of RAM and Flash® memories, other desirable film properties include low threshold voltage for low power applications and a large electrical resistivity contrast between the phases.

We describe here the application of a new high throughput parallel method of thin film synthesis based on UHV MBE technology to the deposition of high purity Ge:Sb:Te over a compositional range beyond that of previous experiments. The results of a number of sensitive and fast characterisation measurements developed for thin film materials are also reported together with high throughput measurement of the optical switching characteristics.

2. EXPERIMENTAL METHODOLGY

2.1 High Throughput Deposition

Conventional chalcogenide thin films can be synthesised via a number of methods most of which require a target or charge material of identical composition to the required film to be analyzed on a sample by sample basis. This in turn requires fabrication of a suitable target or bulk glass, thermal analysis, typically by differential thermal analysis (DTA) and X-ray diffraction to determine amorphicity. In 1991, Ledaudy *et al* [5] undertook an investigation of the amorphous zones in the GeTeSb system, characterizing over sixty individually fabricated samples in this way. Samples were fabricated one by one in a sealed ampoule by melting of the constituent elements and then quenching to form a glass. This process is very time consuming and if one is required to study a whole host of different materials it can also be expensive and impractical.

Our initial attempts to increase the efficiency of the material deposition process were to fabricate graded composition chalcogenide films by using pulsed laser deposition (PLD). This technique was developed in order to deposit sulphur based chalcogenide glass systems which are relatively unexplored for phase change memory applications, but extensively applied in other areas of optoelectronics [6]. Thin films deposited by PLD can vary radially in composition from the deposition's central region therefore it was possible to efficiently evaluate many different chemical arrangements. However the process was limited to compositions close to that of the target material. To fully explore new compositions for phase change applications, a new technique was required which had increased control and a wider composition range. Partnership with the School of Chemistry and Ilika Technologies Ltd provided this capability with a physical vapour deposition system that allows simultaneous "wedge" growth of elements based on UHV molecular beam epitaxy technologies. The system is designed to allow graded composition and morphologies of alloys,

mixed and doped oxides, nitrides and hydrides to be deposited using a combination of both e-beam and Knudson sources and a Plasma Atom Source.

Two HT-PVD synthesis chambers, one allowing up to six individual elemental sources, the other four, are available with an ultra high vacuum (UHV) transfer line between systems and to UHV characterisation chamber. A glove box and fast entry chamber allow clean transfer of samples in and out of the system. It is possible to create both continuous films and with the use of a contact mask, discrete arrays. Combined control of the gradient of material across the sample using wedge shutters for the individual sources, and the rate of deposition from each source, allows complete control of the compositional range of the material: Initial broad composition ranges can be synthesised, with concentrations of individual elements covering ranges from 0 to almost 100%. Following preliminary screening, one can synthesise a much narrower composition range at higher resolution close to regions of interest. In this work we have deposited a broad Ge-Sb-Te composition range, using germanium, antimony and tellurium supplied by Johnson Matthey from their Puratronic® range, with a purity of 99.9999% (metals basis) or better. Substrates were typically silicon or thermally oxidized Si with a 32 mm x 32 mm footprint.

Figure 1 shows the calibration depositions of individual Ge, Sb and Te samples measured by energy dispersive X-ray spectroscopy (EDS) at 100 points over the material and plotted as a contour map. Note that in the direction orthogonal to that of the elemental gradient (determined by the "wedge" shutters, the concentration is constant. The elemental compositions of the material shown in figure 1 ranges between 14- 84 % tellurium, 1 – 24 % germanium and 7 – 77% antimony.

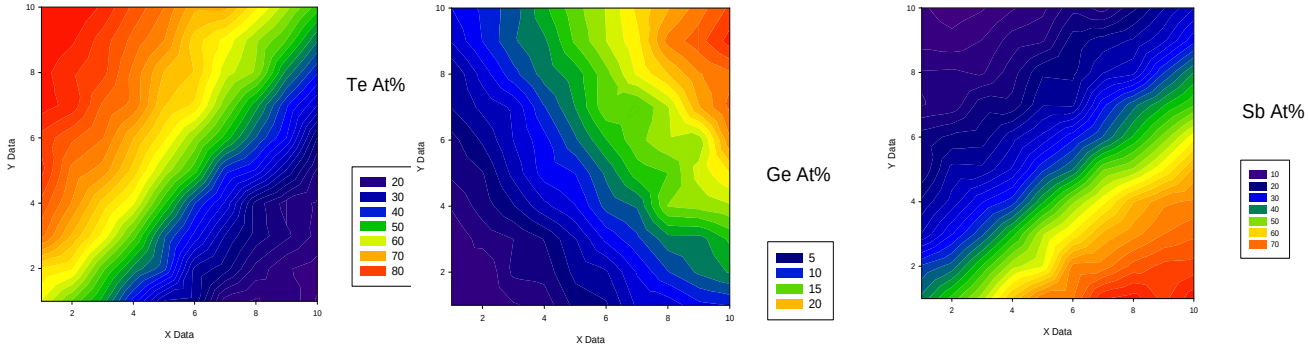

Figure 1. Calibration depositions of the individual elements, representing depositions of between 14- 84 % tellurium (left), 1 – 24 % germanium (centre) and 7 – 77% antimony (right).

To date we have synthesised about 40 samples over a variety of compositional ranges. Figure 2 shows how the combination of just 5 synthesised samples largely covers the complete range of ternary compositions of GeSbTe. For comparison the previously published combinatorial depositions are indicated by the shaded area [4]. A typical time required for deposition once the sources have been calibrated is about 30 minutes. Note that the points represent only the points of analysis (approximately 2 mm apart) on the sample. Measurements can generally be made with most analytical and figure of merit probes with a considerably higher density, providing concomitantly more detail within the ternary space.

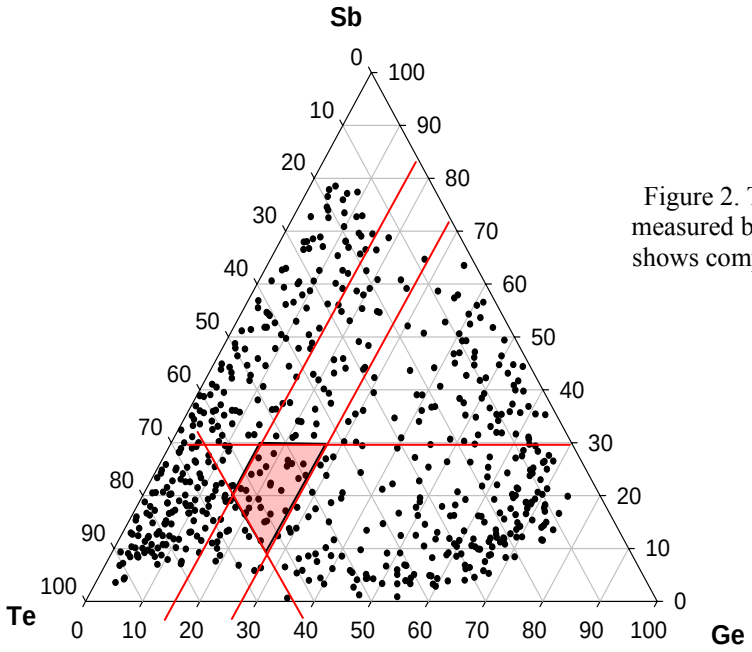

Figure 2. The compositional region covered by 5 samples measured by EDS (100 points per sample). The shaded area shows compositions deposited by combinatorial methods in previous publications [4].

A digitally processed photograph of a typical substrate is presented in figure 3 together with the compositional range measured by EDS. The material is synthesised over the entire area of the substrate in a continuous thin film (ca. 100 nm in thickness). The overlaid white squares represent the regions which would be exposed to deposition if a contact mask was used during synthesis. The EDS measurements were made in the centre of the white squares. Following deposition at a substrate temperature of 300K, it was possible to see by eye a lighter (more reflective) region in the Ge depleted corner of the substrate. It was hypothesised that the more reflective corner was of crystalline nature and this is further discussed in the next section.

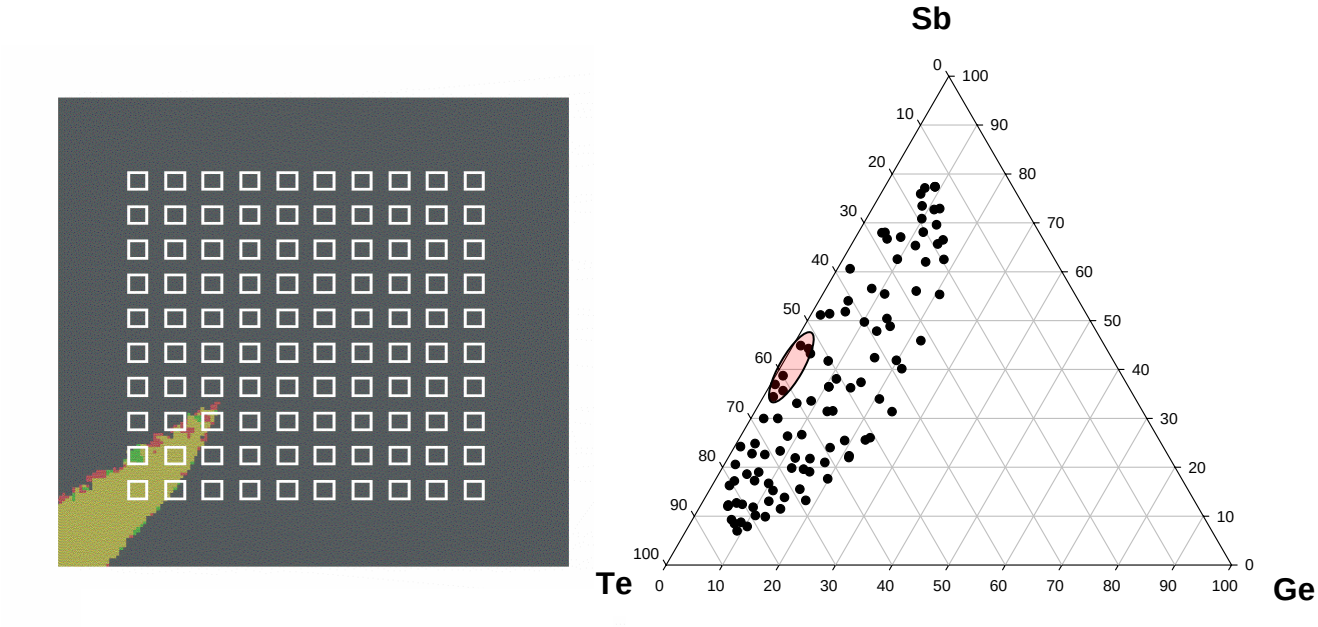

Figure 3. A photograph (left) of the as deposited GeSbTe film, the lightly shaded area at the lower left corresponds to the region of glass formation around 55 – 65 % antimony (shaded region).

2.2 High Throughput Screening and Characterization

High throughput analysis techniques specifically adapted to the characterisation of the structure and composition of thin film materials are required in order to rationalise measured trends in key figures of merit.

Table 2. Summary of in-situ and other high throughput screening methods.

Parameter	Equipment	Specifications
Composition and Structure	Automated SEM and EDS (JEOL JSM-5910; Oxford Instruments INCA 300)	0-30kV, up to 300K magnification (3.0 nm resolution)
	Automated Thin Film XRD (Bruker C2 XRD)	Cu Kα source (λ= 1.54184 Å) 2Θ - 29.4° to 62.4° 60 sec per sample (~100μm spot size)
	Automated Atomic Force Microscopy (Oriel)	Automated Stage, Contact and Non-Contact Modes.
	High Resolution TEM and EDS (JEOL JEM 3010; Oxford Instruments INCA 100TEM)	100-300kV; magnification up to 1.5M, res. 0.21 nm
	Automated Raman Microscopy (Renishaw)	
Conductivity	Automated Four-Point or van de Pauw . (Four Dimensions Inc. Model 280DI)	0.05μΩ cm – 5 KΩ cm (50nm sample).
Optical	Automated Imaging Ellipsometer (Nanofilm Technology I-Elli2000)	100 Δ and ψ ”images” in 20-25 minutes providing refractive index.
Thermal	Thermal Camera	Parallel Measurement of Temperature
Thickness	Profilometer (Alpha Step)	
	Automated Atomic Force Microscopy (Oriel)	Automated Stage, Contact and Non-Contact Modes.

For the chalcogenide materials synthesised in our programme, a number of methods have been selected (Table 2) in order to provide bulk structural, bulk and surface compositional, optical, thermal and conductivity characterisation. With the exception of the surface analytical techniques and thermal measurements which are carried out in an online analytical chamber, analysis is carried out ex-situ. Initial experiments on switching have been carried out using an automated stage, a 3mW 633nm laser combined with an optical microscope. This is the same system as used for Raman Microscopy, the result being that Raman spectra can be obtained from the un-switched (using lower power density) or switched phases. We are also in the process of developing a number of chip based screening techniques to investigate switching by Joule heating, and a number of other optical screens for the investigation of optical switching.

3 RESULTS AND DISCUSSION

Figure 4 shows the EDS analysis and optically processed image of a masked Ge:Sb:Te thin film sample. The contact mask is used to produce discrete fields for “on chip” screening measurements (not shown). EDS measurements have been made at 100 points in the centre of the masked fields. These compositional points are plotted in the ternary map in Figure 5. This sample is restricted to the

low Ge (0-10 at. %) atomic compositional region across a wide range of Te (18-96 at. %) and Sb (5-80 at. %) compositions.

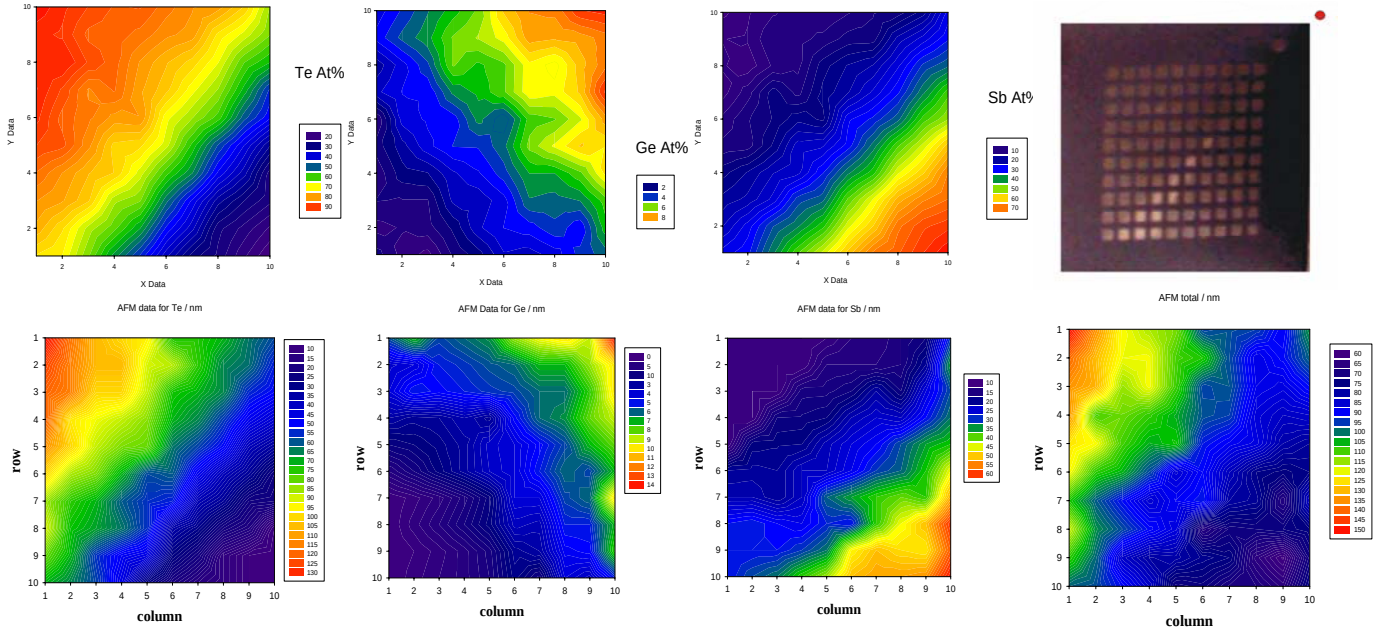

Figure 4 EDS (at. Composition) and AFM (thickness/nm) contour maps of the masked Ge:Sb:Te sample shown in the processed optical image. The total thickness of the fields measured by AFM is also shown.

In addition to the EDS measurements, AFM measurements are also presented in the form of contour maps. The mask and deposition technique allows the independent measurement of the three deposited components in each field. The sum of the three components clearly gives the total thickness of the Ge:Sb:Te fields. Note that the contour maps of the AFM measurements reflect the characteristics of the deposition method, and of course are consistent with the compositional maps produced by EDS. The total thickness of the fields varies in the range 60-150 nm. A consequence of synthesising a wide range of material composition results in a concomitant variation in thickness simply as a result of the density of the material. Interpretation of key figure of merit or optical properties therefore requires a systematic measurement of sample thickness together with the compositional map.

The processed image of the sample in figure 4 clearly shows fields which in fact appear lighter (more reflective) to the naked eye. The compositions which correspond to the more reflecting phases are shown by the red points in the ternary map of figure 5. In order to establish the structural characteristics of the "as deposited" material, XRD measurements have also been made of all 100 fields. A subset of these is shown in figure 5. The series shown correspond to the second row of fields from the bottom of the image in figure 4. Typical XRD measuring times for each fields was 600s. Most of the fields appear to be highly amorphous, with the clear exception of (3,2) and (4,2) which correspond to the to highly reflective fields along the row. Similar XRD results are obtained for the crystalline phase identified in the continuous sample shown in figure 3. This supports our interpretation that the enhanced reflectivity is a result of a crystalline phase. The compositional region

in which the phase is produced is around Te60:Sb40 (towards the limit of no Ge) and would logically correspond to the Te_3Sb_2 phase. It is in this region that crystallization activation energies are lowest.

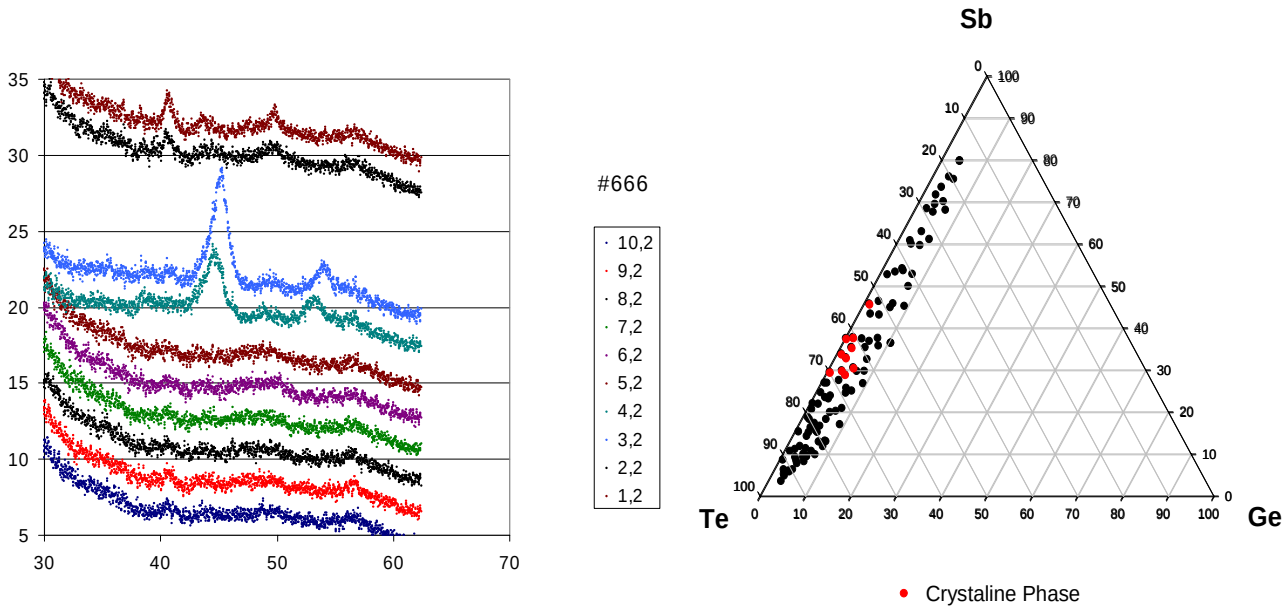

Figure 5. The ternary composition of the field in the Ge:Sb:Te sample shown in Figure 4. The red points indicate fields which appear to be crystalline in phase in the processed optical image. A series of XRD measurements are shown which clearly demonstrate the transition between an amorphous and crystalline phase. The co-ordinates (x,y) are defined with (1,1) corresponding to the field in the left hand bottom corner .

Figure 6 shows the results of the ellipsometric measurement of Δ and Ψ (degrees) measured at 633 nm for the 100 fields shown in the sample in figure 4 plotted in the form of a contour map. The ellipsometric angle Δ primarily reflects the difference in thickness of the material, which can be substantiated by comparison with the thickness data from AFM (Figure 4). The ellipsometric angle Ψ is dominated by the absorbance of the phase. Comparison of the map of Ψ with the processed optical image clearly shows the correlation of Ψ with the highly reflecting crystalline phase. A full evaluation of the optical constants, n and k, is now in progress and will be reported separately.

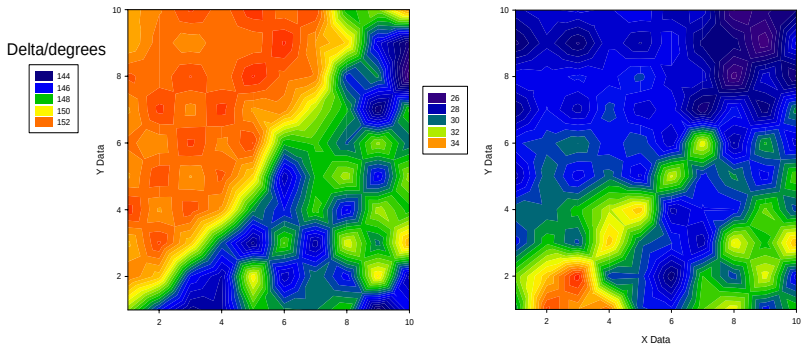

Figure 6. Raw data from automated ellispsometric measurements of Δ and Ψ (degrees)

Additional analysis also in progress includes conductivity measurements, also automated, using a four-point over a resistivity range of 0.05mΩ cm – 5 KΩ cm. This data is presented in figure 7.

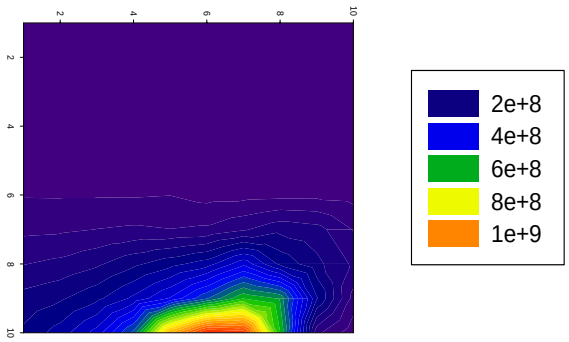

Figure 7. Four-point probe conductivity measurement mapped from 100 data points

4. CONCLUSIONS

We have shown that the application of a novel high throughput deposition method can be used to deposit wide compositional ranges of pure chalcogenide materials, specifically GeSbTe. Combined with a range of fast characterisation and screening methods, the phases and behaviour of the materials as a function of composition can be screened rapidly and with confidence. With the wide variety of potential ternary chalcogenide phases available, and the even wider ranges of doped materials, the flexibility and controllability of the high throughput synthesis makes it an ideal tool for the discovery of mew phase change materials.

5. ACKNOWLEDGEMENTS

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Biographies

Dan Hewak leads a research group investigating novel glasses for optoelectronic devices. He obtained his PhD from the University of Waterloo, Canada, in 1989, where he studied waveguide optics. Since 1991 he has been with the ORC where he has
developed a broad range of experience in new glasses, and in particular sulphide glasses, for optoelectronic applications. This work has led to the first chalcogenide glass laser and the first single mode fibre in a gallium lanthanum sulphide glass. This work has been in collaboration with industrial and university partners worldwide. He has published over 100 papers and conference presentations and is the holder of five patents for novel glasses and their applications. He has presented his work internationally as both invited and contributed talks. He is the editor of a text, published in the EMIS Data review series by the IEE entitled Properties, Processing and Applications of Glass and Rare-Earth Doped Glasses for Optical Fibres and section editor for Optical Materials in the journal Current Opinion in Solid State Materials.

Brian Hayden is Professor of Physical Chemistry in Southampton. After obtaining a PhD in Physical Chemistry in Bristol in the field of Surface Science, he worked as a postdoctoral fellow at the Fritz Haber Institute der MPG from 1979 to 1984 developing surface sensitive optical measurement (spectroscopic ellipsometry and infra-red (RAIRS) for the investigation of adsorbates). He was a lecturer at the University of Bath, and moved to the University of Southampton in 1989 where he was appointed to a personal chair in 1994. His main areas of research are surface science, model heterogeneous catalysis, electrocatalysis and surface electrochemistry, fuel cell catalysis and high throughput materials chemistry. The methodologies developed in high throughput materials discovery are a key component of a new University of Southampton "spin-out" company, Ilika Technologies, operating in the area of High Throughput Materials Research (BEH is a founding member).

Sam Guerin Since 2001 Samuel has been a key member of the team which has developed Ilika's high throughput thin film technology. Samuel holds degrees equivalent to a BSc and an MSc in Physics from the University of Tours, an MSc in Material Science from the University of Bordeaux and a PhD in Electrochemistry from the University of Southampton.

Rob Simpson commenced his PhD in October 2003 after graduating from the University of Bath with a degree in Physics and spending a year in the high power fibre laser and amplifier research group at Nortel Networks. His research is centred on the phase change properties of chalcogenide glasses (glasses containing sulphur, selenium or tellurium). He has successfully found new materials that can be switched electrically and optically between amorphous and crystalline states. In March of this year he was awarded the Westminster Medal for excellence in research at the 7th annual reception for Britain's younger Scientists, Engineers and Technologists (SET for Britain) at the House of Commons.

Graeme Purdy has worked in the field of high throughput methodologies for materials research for a little over five years. As CEO of Ilika, Graeme's work has revolved around the use of novel high throughput techniques for materials discovery and characterisation, with an emphasis on applying research techniques to discover breakthrough new materials. Prior to joining Ilika, Graeme was a director of Avantium in the Netherlands. Graeme holds degrees in Natural Sciences and Chemical Engineering from Cambridge, UK and an MBA from INSEAD business school in France.