Thermally Stable, Low Current Consuming Gallium and Germanium Chalcogenides for Consumer and Automotive Memory Applications

D.W. Hewak, C.C. Huang, B. Gholipour and F. Al-Saab
Optoelectronics Research Centre, University of Southampton, Southampton, SO17 1BJ, United Kingdom
Contact email: [Dan Hewak] dh@orc.soton.ac.uk

S. Guerin, A. Anastasopoulos*, B. Hayden* and G. Purdy
Ilika Technologies Ltd, Kenneth Dibben House, Chilworth, Southampton, SO16 7NS, United Kingdom

*also with, *School of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom*

ABSTRACT

The phase change technology behind rewritable optical disks and the latest generation of electronic memories has provided clear commercial and technological advances for the field of data storage, by virtue of the many well-known attributes, in particular scaling, cycling endurance and speed, that chalcogenide materials offer. While the switching power and current consumption of established germanium antimony telluride based memory cells are a major factor in chip design in real world applications, often the thermal stability of the device can be a major obstacle in the path to the full commercialization. In this work we show that phase change media based on the gallium and lanthanum chalcogenides can outperform the well know benchmark performance of germanium antimony telluride devices. Facilitated by high throughput screening of gallium lanthanum sulphides and tellurides, we show these compounds offer set and reset currents over an order of magnitude lower, than an equivalent germanium antimony telluride device, while at the same time offering improved thermal stability and the potential for improved endurance. In addition we introduce the fabrication of germanium antimony based materials fabricated by chemical vapour deposition and show phase change functionality in these materials. Work is in progress to fully characterize the phase change characteristics of these materials at both room temperature and elevated temperatures however preliminary results show that Ga:La:S based devices continue to show the ability to display a measurable threshold above 250^{o}C.

Key words: chalcogenide, phase change memory, thermal stability, threshold voltage, set and reset currents.

1. INTRODUCTION

Our particular interest in the field of phase change memory (PCM) is the discovery of new chalcogenide alloys to potentially outperform the commonly used Ge:Sb:Te (GST). There is a wide range of chalcogenide alloys, range from pure chalcogenides, to pnictogen-chalcogen, tetragen-chalcogen, metal chalcogenides to halogen-chalcogenides [1]. Many of these compounds are covered within high-level patent literature, within which a vast array of potential compounds suitable for phase change memory are proposed, yet with relatively few studied in detail [2]. Indeed, even among phase change memory cells fabricated with the most conventional GST compounds, the reasons why these compositions provide us with useful and attractive physical properties are still veiled [3]. It is therefore our belief that the field and material space is ripe for a thorough analysis of the compositional space to provide both a better understanding of the range of properties the numerous chalcogenide alloys offer and to optimize the compositions to meet the demands of practical solid state memory.

It has been indicated that GST based phase change memory devices with a high level of scaling may suffer from very poor thermal stability [4]; moreover as applications of GST based memory cells extend to harsh operational environments such as aerospace and automotives, device performance as temperatures fluctuates will be compromised. These factors along with high current consumption of memory cells based on this alloy pose the biggest obstacle in realising the full commercial potential of PCRAM. Improved stability has already been obtained using Ge-doped Sb:Te [5] and also by replacing Ge completely by Ga [6] and this allowed device operation at 100^{o}C.

In the work presented here we fully explore the relatively unknown gallium and lanthanum based chalcogenides with a particular focus on both performance and temperature stability.

2. MATERIALS

In the past year, we have applied high throughput methodology to synthesize and characterize a range of chalcogenide glass families based on Ga:La:S and Ga:La:Te as as well as the benchmark Ge:Sb:Te (GST) family. In addition, Ge:Sb and Ge:Sb:S were deposited and characterizated. These germanium based phase change materials were deposited by chemical vapour deposition (CVD) using inorgancic precursors. Our work with the GST phase change material was used as a control standard with which the electrical and thermal properties of relatively more novel compositions could be compared.

For the Ga:La:Te, which inherently offer higher thermal stability the full ternary was deposited by physical vapour deposition and all compositions on the phase diagram were screened using high throughput techniques, For the first time, Ga:La:Te alloys were deposited and glass formation demonstrated over the majority of the phase diagram [7]. Particular promise was obtained with compositions containing a relatively high proportion of Te and Ga to La, where resistivity measurements revealed four order of magnitude difference between the glass and crystalline phases (see figure 1). It could also be shown that the average temperature of the amorphous to crystalline phase transition was 50-100K higher for these phases over standard GST composition.

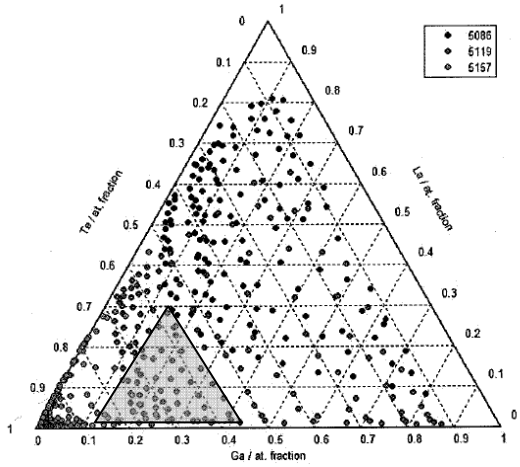

Figure 1. Compositional spread of the Ga:La:Te glass system characterized by high throughput screening methods. The shaded area identifies a region exhibiting crystalline to amorphous phase transition exhibiting a resistance difference of over four orders of magnitude.

Gallium lanthanum sulphides were deposited from elemental precursors by thermal and e-beam evaporation respectively. A compositional gradient of approximately 5% to 90% gallium and 95% to 10% lanthanum was achieved on a single substrate. Sulphur was incorporated in the film using a K-Cell as a source and a “hot lip” molybdenum cracker to break the larger sulfur chains to mono or di-Sulfur. This allows a smooth and more controlled deposition of sulphur. Post processing at temperatures up to 700^{o}C resulted in stoichiometric Ga_2S_3:La_2S_3 across the compositional gradient.

In both of these two material groups, synthesis took place using ultra high vacuum (10-9 Torr) and molecular beam epitaxy based technology in high throughput physical vapour deposition chambers (HT-PVD). Ilika Technologies Ltd provided this capability with a system allowing up to six individual elemental sources, the other four, are available with an ultra high vacuum (UHV) transfer line

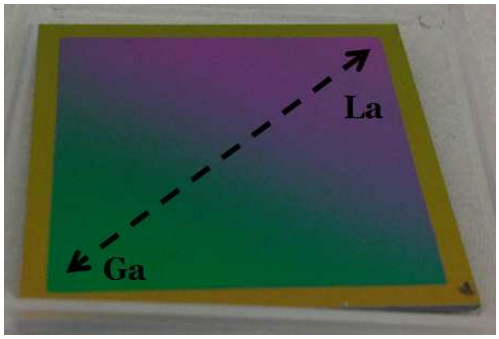

Figure 2. Photograph of a typical Ga:La compositional array prior to sulphurization and post processing.

between systems and to UHV characterization 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. Substrates were typically silicon or thermally oxidized Si with a 32 mm x 32 mm footprint. A number of sensitive and fast characterisation measurements developed for thin film materials were used for film charactization and high throughput measurement of the switching characteristics.

Germanium antimony (Ge-Sb) thin films with tuneable compositions have been fabricated on SiO_2/Si, borosilicate glass, and quartz glass substrates by chemical vapour deposition (CVD). Deposition took place at atmospheric pressure using metal chloride precursors at reaction temperatures between 750 and 875 ^oC. [8]. To simplify the processing, we used fixed gas flow rates of $GeCl_4$, $SbCl_5$ and 6 % H_2 /Ar of 50 – 200 ml/min. By simply changing the reaction temperature at zone T_1, the ratio of Ge to Sb in the deposited Ge-Sb film could be varied. In this process, Sb acted as the base material or host and Ge acted as the dopant in the Ge-Sb thin films. Therefore, the higher the temperature of the CVD reaction, the greater the content of germanium could be incorporated in the Ge-Sb thin film.

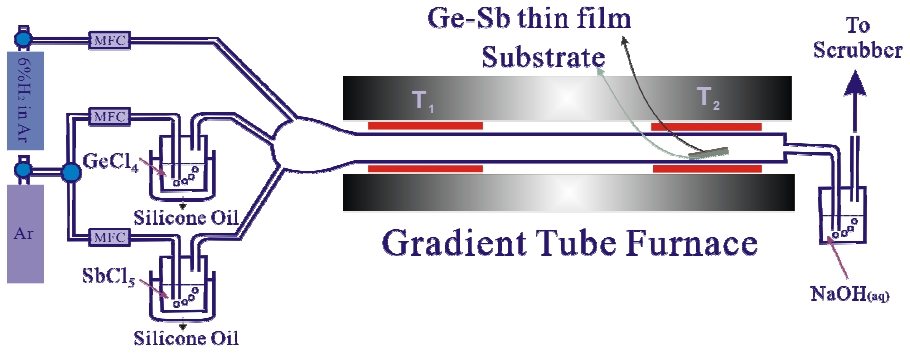

Figure 3. Schematic diagram of the chemical vapour deposition apparatus used for the fabrication of Ge:Sb thin films.

3. METHODOLOGY AND RESULTS

A series of devices were fabricated using standard photolithography, reactive ion etching, ion beam milling and ion beam deposition to yield the device structure shown schematically in Figures 4. A total of 100 individually addressable cells of varying sizes were fabricated in each of the compositions 13Ga:7La:30S and 2Ge:2Sb:5Te. Devices were fabricated on a SiO2/Si wafer on which the Ga:La:S or Ge:Sb:Te was deposited by RF sputtering. For the Ga:La:S films, the sputtering targets were fabricated in-house by melt-quenching gallium sulphide and lanthanum sulphide powders in a vitreous carbon crucible. The Ge:Sb:Te sputtering targets were obtained commercially (Testbourne Ltd. UK) and were nominally of the composition Ge2Sb2Te5 (atomic %). Compositional analysis by energy-dispersive X-ray spectroscopy (EDX) confirmed this ratio of elements. A Kurt J. Lesker

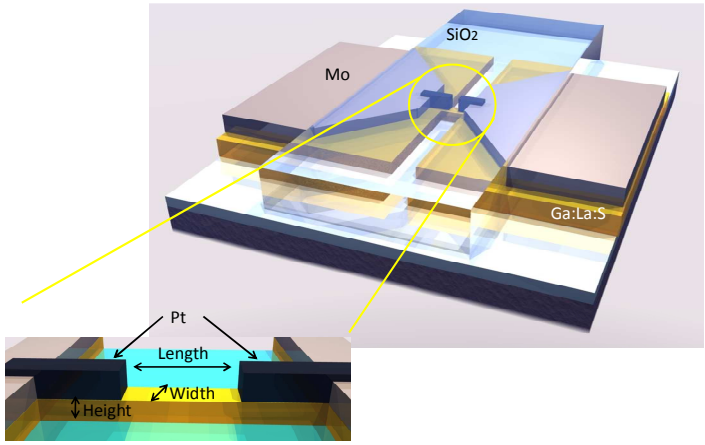

Figure 4. Schematic of the prototype memory cell, based on a lateral design, showing in the inset detail of the chalcogenide (Ga:La:S or Ge:Sb:Te) stripe capped with two platinum electrodes. Memory cell dimensions ranged from 50 – 300 nm length, 15 – 75 nm height and 40 – 375 nm width.

NANO38- SPUTTER thin film deposition system with a background pressure of 8 x 10^{-5} Torr was achieved before the sputtering began. High purity argon was used as the sputtering gas and the distance between the target and the substrate was 150mm. The substrate was kept at room temperature initially and minimal <10^{o}C temperature increase was observed while the film was being formed. For the Ga:La:S, the deposition power used was 60W and the argon gas flow was 15cc. For Ge:Sb:Te, the deposition power used was 45W and the argon gas flow was 37cc/min.

The film thickness were confirmed using a KLA Tencor P16 Stylus Profiler. Film thicknesses of 15, 30 and 75 nm were used in both materials in the final devices.

Trenches were etched in the chalcogenide layers were etched to obtain the desired nanowires. These isolated nanowires were created using ion beam milling of the chalcogenide layer to obtain restricted nanowires of different geometries. The resulting nanowires ranged from 40 to 375 nm in width and 50 – 300 nm in length.

Electrical contacts were provided by molybdenum metal pads which were deposited by sputtering using the process described earlier. The substrate was kept at room temperature and the deposition power used was 100W, with argon gas flow of 15cc. The contacts were patterned using photolithography using a positive photoresist (S1805) and the lift-off technique with a pre-deposition Oxygen plasma ash (using a 100W plasma power and 10cc Oxygen flow), The ashing was also repeated post lift-off to clean the samples of any residue photo resist. The deposition power used was 45W and the argon gas flow was 37cc. Platinum electrodes were then created using electron-beam assisted Platinum deposition using a FEI Helios 600 Focused Ion beam. The gap between these electrodes formed the final nanowire or memory cell. An SEM image of a typical cell is shown in Figure 5.

A similar design for the Ge:Sb devices was used, in which a total of 10 cells were fabricated in the eutectic composition 15Ge:85Sb. A scanning electron microscope image of one of these cells is shown in Figure 6. In preliminary tests each material family provided clear phase change functionality.

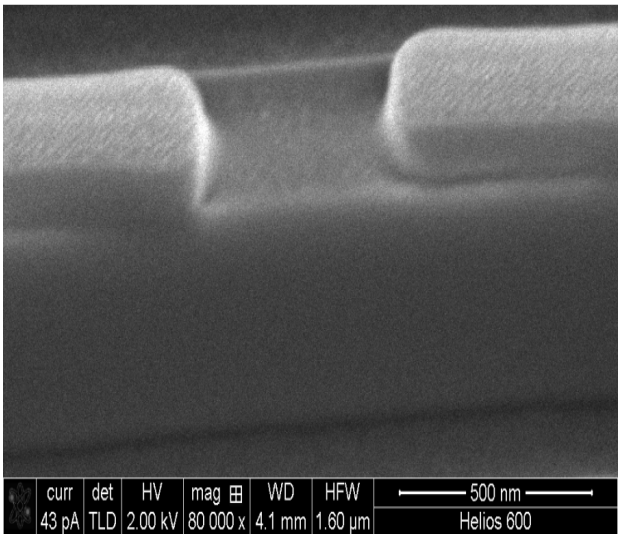

Figure 5. Scanning electron microscope (SEM) image of Ga:La:S memory cell formed from two platinum electrodes spaced 375 nm apart. The chalcogenide layer has been milled away to form the nanowire cell.

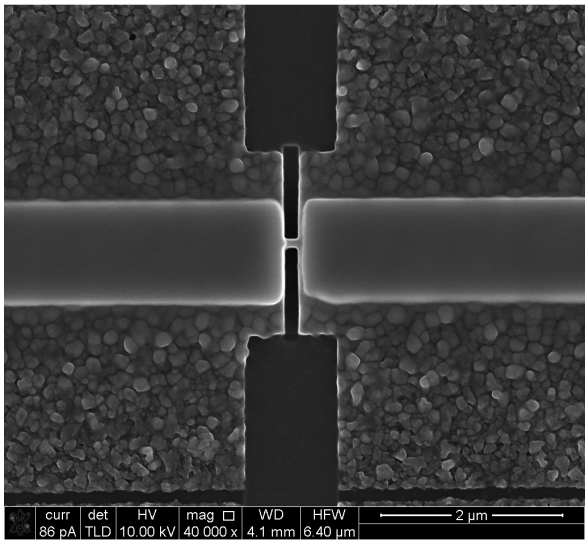

Figure 6. SEM image of a Ge:Sb nanowire memory cell. The Ge:Sb is deposited by chemical vapour deposition and following reactive ion etching, a cell 100nm x 150nm x 100nm thick was achieved.

The electrical characterization of all devices was carried out with the probe station setup consisting of an Agilent 4155C semiconductor parameter analyzer, as well as an Agilent 8110A dual pulse generator. By introducing voltage sweeps and measuring the current across the fabricated cell using the source measure unit within the semiconductor parameter analyzer, each cell was characterized. It should be noted that an internal load resistance within the instrument provides current limitation in order to protect the device. The I-V characteristics of a typical

Ga:La:S cell are shown in Figure 7. The resistance of the material in its crystalline state was on the order of ~3 x 10^9 Ω. Once the voltage was increased above the threshold, the resistance switches to a more conductive state showing a resistance of ~ 3 x 10^5 Ω. The second sweep demonstrated that the changes were stable and the film remained in a high conductivity low resistance state as a result of the first sweep. The electrical switching was reproducible, though our tests limited switching to only 10 cycles for these devices, however endurance cycling on a larger thin film device cycled ~ 10^6 times without failure [9]. The resistance contrast between two phases was on the order of four orders of magnitude; therefore this result would indicate promise for PCRAM applications.

A more detailed and statistical study of SET and RESET operations was made on approximately 50 cells in each of the Ga:La:S and Ge:Sb:Te designs. Pulse widths for the SET were set to be in excess of the expected switching time, typically 200ns ns, and the threshold voltage was measured for the SET and RESET function. This data was plotted as a function of cell area, ie, the active area of the chalcogenide between the platnium electrodes and representative data is shown in Figure 8 and 9. Despite some overlap in the data at small cell sizes for the SET operation it is clear that there is a difference in the performance of the two materials when used in identical cell designs. A curve was fit to each set of data, for which N, the number of cells measured, varied from 20 to 50. To allow a direct comparison of performance of the two materials, a cell area of 12 x 10^{-6} nm^2 was chosen. This is above the region of small cell sizes where our experimental uncertainty was relatively large, but significantly smaller than the largest of the cells we fabricate, some of which were an order of magnitude larger. The results of this comparison are shown in Table 1 below.

The results indicate that there is an enhancement of the resistance contrast of approximately an order of magnitude with Ga:La:S offering a ~10^4 difference between the amorphous and crystalline states. This is due, in part from the relatively large resistance in the glassy state (~3 x 10^9 Ω), which manifests itself also in a slightly higher threshold voltage. A more thorough study of the interpretation of these results is currently underway.

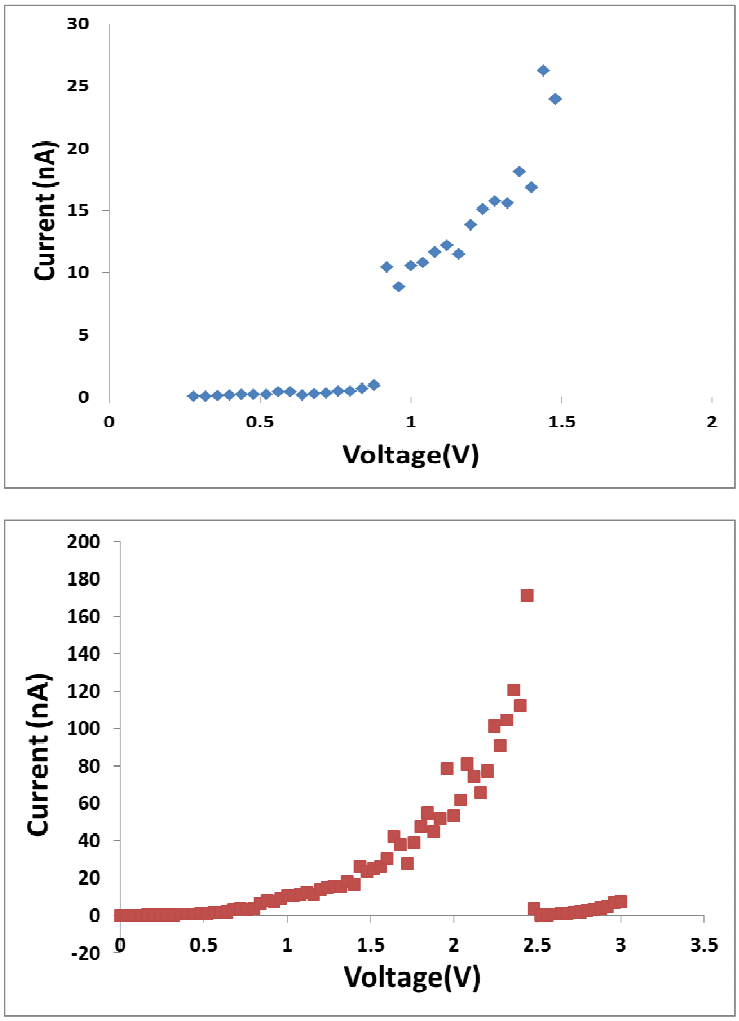

Figure 7 Switching characteristics of a typical Ga:La:S cell, showing the I-V curve during switching from the glass to amorphous phase (top image) and the reversible switching back to the amorphous phase (lower image). The set and reset voltages were 0.92V and 2.44 V, respectively.

Table 1. Comparison of switching characteristics for Ga:La:S and Ge:Sb:Te memory cell. In both cases the cell area is 12 x 10^{-6} nm^2 and measurements were made a room temperature. The composition of the alloys were 13Ga:7La:30S and 2Ge:2Sb:5Te

Alloy	Set Current (μA)	Reset Current (μA)	Threshold Voltage (V)	Reset Voltage (V)	Switching Power (μW)	Cell Resistance Amorphous (Ω)	Cell Resistance Crystalline (Ω)	Resistance Ratio
Ga:La:S	3.49 ± 1.44	9.17 ± 2.2	3.24 ± 0.17	4.86 ± 0.30	11.3 ± 7.3	3.24 x 10^9	2.85 x 10^5	1.14 x 10^4
Ge:Sb:Te	116 ± 40	175 ± 65	2.22 ± 0.13	3.41±0.19	257 ± 104	2.22 x 10^7	2.02 x 10^4	1.10 x 10^3

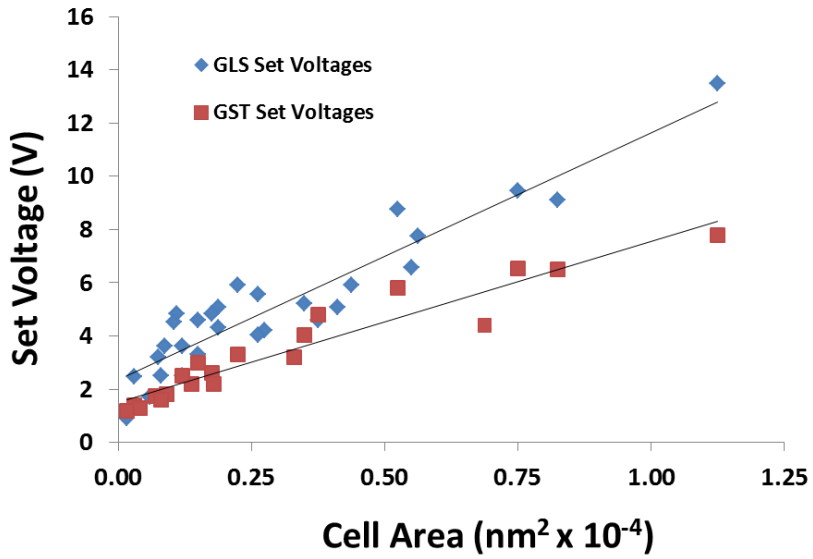

Figure 8. SET Voltage as a function of cell area for Ga:La:S and Ge:Sb:Te phase change test devices. The SET Voltage was determined from the point on the IV curve at which the current increased significantly indicated a transition from glass to crystalline phase. A line of best fit was determined through a least squares fit to all experimental cells measured apart which showed switching behavior.

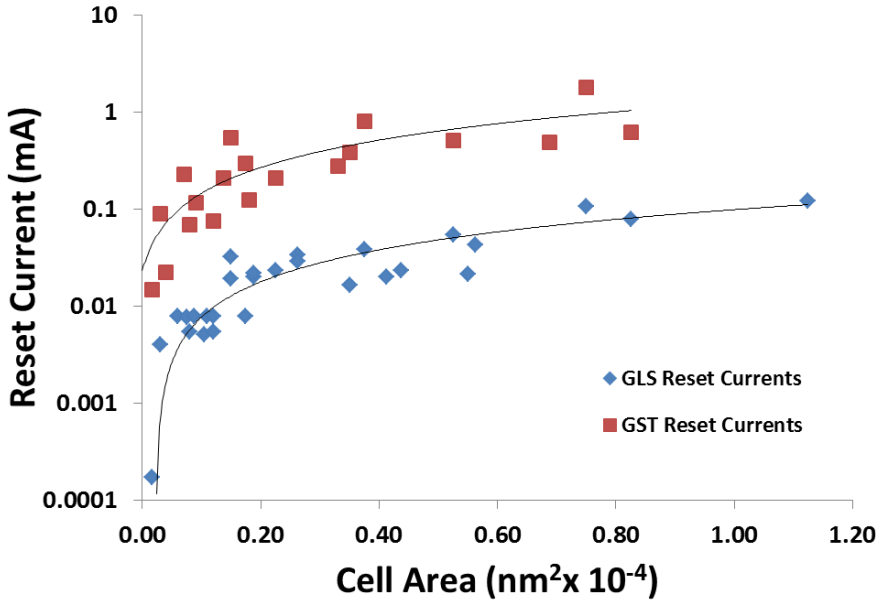

Figure 9. RESET current as a function of cell area for Ga:La:S and Ge:Sb:Te phase change test devices. The RESET current was determined from the point on the IV curve at which the current flow descreased significantly indicated a transition from the crystalline to glass phase. A line of best fit was determined through a least squares fit to all experimental cells measured apart which showed switching behavior.

The Ga:La:S family of chalcogenide glasses are well know to be amongst the most thermally stable chalcogenide compounds offering characteristic temperatures several hundred degrees above other sulphide based compounds [10]. Table 2 compares the glass transition temperature, onset of crystallization and onset of melting for the three chalcogenide compounds which make up this current study.

Table 2. Thermal characteristics of bulk chalcogenide alloys used in memory cell fabrication, all measured in ^{o}C.

Alloy	Glass Transition (T_g)	Onset of Crystallization (T_x)	Onset of Melting (T_m)
13Ga:7La:30S	550	640	830
15Ge:85Sb	-	260	650
2Ge:2Sb:5Te	350	160	610

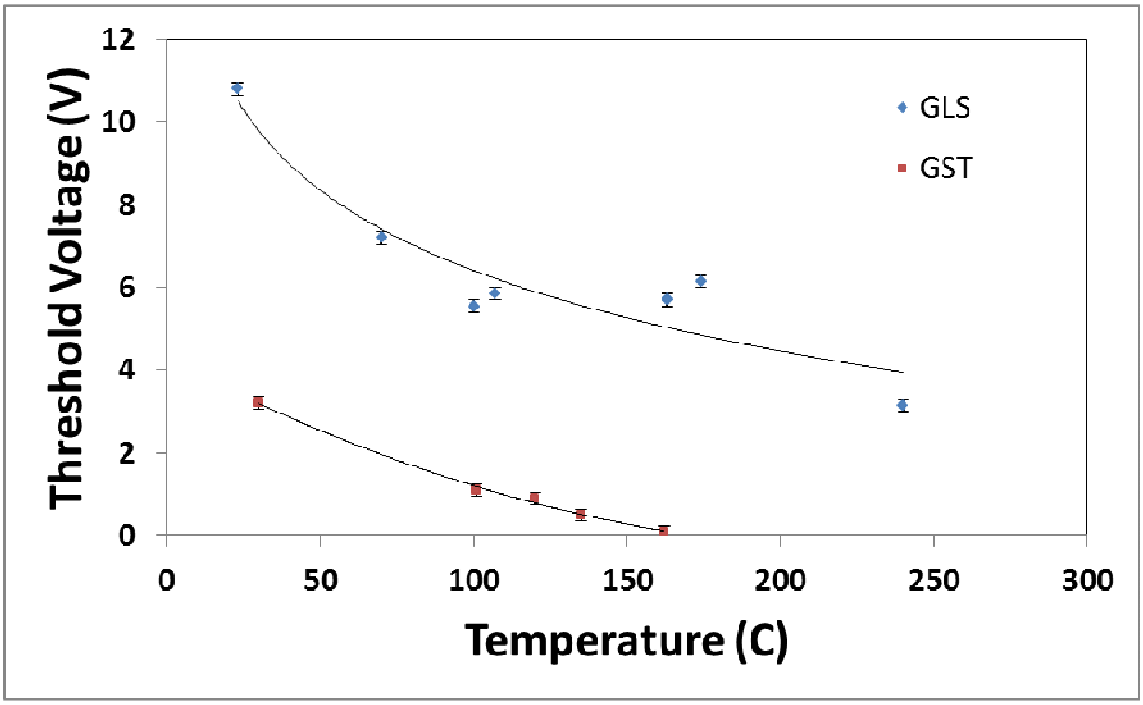

Figure 10. Preliminary data on the temperature dependence of the threshold voltage of a Ga:La:S and Ge:Sb:Te based memory cell. In both cases cells of identical structure were used. The active area of the cell was 10 µm x 10 µm x 70 nm. Note that the cell design for these measurements was of a different geometry and considerably larger than those used for the previous data shown in Figures 7 thru 9.

To assess device performance at elevated temperatures, a series of device based studies have been conducted with both Ga:La:S and Ge:Sb:Te devices. This work will continue with cells from the same fabrication batch as was used to assess SET and RESET conditions of the two alloys, and will include data for the Ge:Sb cells in addition. The preliminary results we show here indicate that in accordance with the characteristic thermal properties there is a clear improvement in onset of failure, defined here, as the loss of threshold switching, in the two materials. Figure 10 shows shows a typical measurement in which the threshold voltage as a function of temperature is plotted for both a Ga:La:S and Ge:Sb:Te device. For the Ge:Sb:Te device, loss of threshold switching occurred at approximately 160^{o}C whereas for the Ga:La:S sample, repeatable threshold switching continued to 250^{o}C. Although this data only indicates enhanced temperature operation in a prototype device rather than real world application, it does clearly indicate that significant difference in temperature stability can be achieved through compositional modification.

4. SUMMARY

We have fabricated a number of phase change memory test cells in the form of nanowires on the order of 15 – 375 nm in dimension. Gallium lanthanum sulphide based devices were fabricated and compared to germanium antimony tellurite devices of an identical structure. Gallium lanthan sulphide based devices outperformed germanium antimony telluride devices on a number of key parameters. In addition, binary germanium antimony devices in which the phase change alloy was deposited by chemical vapour deposition were demonstrated. We reveal enhanced temperature stability in phase change alloys identified through high throughput screening of families of chalcogenide alloys. Work in progress is fully quantifying this range of chalcogenides to provide optimized materials for commercial memory based devices.

5. REFERENCES

1. Stephen R. Elliott, Chalcogenide Glasses, ***Volume 9 of Materials Science and Technology***. VCH, 1991.
2. Semyon D. Savransky, Tz-Chin Wei, Triz Analysis of US Patents in Ovonic Phase Change Memory**, *Journal of Ovonic Research*** Vol. 1, No. 3, June 2005, p. 31 – 37.
3. Junji Tominaga, Robert Simpson, Paul Fons, and Alexander Kolobov , Phase Change Meta-material and Device Characteristics, ***EPCOS'10***, Milan Italy (2010)
4. C Wang et al, "Phase-Change Characteristics and Thermal Stability of GeTe/Sb2Te3 nano composite Multilayer Films", **Jap. J. App. Phys.** 48 (2009) 115505
5. Z Wu et al, "Improved stability of a phase change memory device using Ge-doped SbTe at varying ambient temperature", **App. Phys. Lett**. 96 (2010) 133510
6. European Patent Number 1969602, Phase Change Memory Materials, Devices and Methods, 24 March 2010.
7. R.E. Simpson et al, "High throughput synthesis of chalcogenide materials for data storage", ***EPCOS'05*** Cambridge (2005)
8. C.C. Huang et al, **"**Optical properties of CVD grown amorphous Ge-Sb-S thin films ***J.Non-Crystal***. *Sol.* 356 281 (2009)
9. Z. Samson et al , "Metamaterial electro-optic switch of nanoscale thickness", ***Appl. Phys. Lett.*** 96, 143105 (2010)
10. D.W. Hewak et al, "Chalcogenide glasses for photonic device applications", in ***Photonic Glasses and Glass-Ceramics***, Editor Ganapathy Senthil Murugan, Research Signpost, Kerala, India, (2010).

Biographies

Professor D. Hewak is head of the Novel Glass Group at the ORC and an international expert and innovator in the synthesis and application of chalcogenide materials. He works on the purification and synthesis of chalcogenide materials, glass melting and the fabrication of optical fibres, thin films, microspheres and nanoparticles and collaborates with industrial partners and universities worldwide. He has published over 160 refereed papers, is the holder of eleven patents, edited a book on Processing and Applications of Glass and Rare-Earth Doped Glasses for Optical Fibres (IEE) and he is section editor for Optical Materials in the journal Current Opinion in Solid State Materials.