

# Scanning Probe-based Phase-Change Terabyte Memories

C D Wright<sup>1</sup>, M Armand<sup>2</sup>, M M Aziz<sup>1</sup>, H Bhaskaran<sup>3</sup>, B C Choo<sup>1</sup>, C Davies<sup>4</sup>, M Despont<sup>3</sup>, S Gidon<sup>2</sup>, M Klein<sup>5</sup>, O Lemonnier<sup>2</sup>, A Maisee<sup>2</sup>, A Pauza<sup>4</sup>, M Salanga<sup>5</sup>, A Sebastian<sup>3</sup>, L Wang<sup>1</sup>, M Wuttig<sup>5</sup>

<sup>1</sup> *School of Engineering, Computing and Mathematics, University of Exeter, EX4 4QF, UK*

<sup>2</sup> *CEA-LETI, MINATEC, 17 Rue des Martyrs, 38054 Grenoble, France*

<sup>3</sup> *IBM Zurich Research Laboratory, 8803, Rueschlikon, Switzerland*

<sup>4</sup> *Plasmon, Whiting Way, Melbourn Royston, SG8 6EN, UK*

<sup>5</sup> *RWTH Aachen University, Department of Physics (IA), Aachen, Germany*

Contact e-mail: David.Wright@exeter.ac.uk

## ABSTRACT

In this paper we report on recent phase-change research from the EU FP6 project ProTeM (Probe-based Terabit per square inch Memory) that aims to develop scanning-probe based storage media and systems suited to archival and back-up storage applications, with storage densities in the range 1 to 10Tbits/sq.in. and high write/read speeds. In particular we discuss the design and characterisation of new phase-change materials suited to write-once and re-writable probe-based storage, as well as new approaches to the self-assembly of phase-change materials for the production of patterned phase-change media. We also report on the important issue of tip wear when using electrical nanoprobes in contact with phase-change media, and describe new tip designs for the mitigation of tip wear effects.

**Key words:** scanning probe storage, phase-change memories, ProTeM

## 1. INTRODUCTION

Data storage roadmaps are looking towards density targets of around 1 Tbit/sq.in. by 2010 and to 10Tbits/sq.in and beyond thereafter. For magnetic hard disk based storage, because of the well-known superparamagnetic ‘limit’, such a target requires significant research and development both in terms of recording materials and system design. In optical disk storage, due to the optical diffraction limit, achieving such a high storage density also remains difficult. It is therefore timely to investigate alternative storage technologies. A key requirement for any viable alternative Tbit/sq.in storage method is the ability to reduce the interaction volume between the ‘head’, used for the writing and readout, and the storage medium. Such a tool can be found in scanning probe microscopy where a sharp scanning tip is used to detect and modify on the nanoscale some physical material property. Indeed, IBM has already demonstrated the concept of using scanning probe-based techniques for storage devices in their ‘Millipede’ system, where a thermo-mechanical probe is used to write, read and erase indentations in a polymer media [1, 2]. Other promising storage media suited to scanning probe-based technology include phase-change materials, where the electro-thermal writing and electrical reading of nanoscale ‘bits’ has already been achieved [3-5], and ferroelectric materials [6].

In this paper we report on recent phase-change research from the EU FP6 project ProTeM (Probe-based Terabit per square inch Memory - see <http://www.protem-fp6.org>) that aims to develop scanning-probe based storage media and systems suited to archival and back-up storage applications. The archival sector is becoming increasingly important, due to introduction of new legal requirements governing the storage of governmental and commercial data, and due to the ever-increasing amount of digital data generated by all aspects of our everyday life. Indeed, it has been estimated that the total archival capacity required world-wide will exceed 20 ExaBytes (20 x10<sup>18</sup> bytes) by 2010 and 60 ExaBytes by 2013, generating market values of in excess of \$20 billion and \$30 billion respectively. For archival applications reliability, data integrity and media longevity (in both write-once read-many (WORM) and re-writable (R/W) formats) feature much more prominently than in other storage sectors and professional archiving addresses different cost/performance requirements compared to standard consumer applications. ProTeM aims to meet all these archival requirements (density, capacity, data rate, longevity...) through the use of scanning probe-based technologies.

Typical specifications, from a user-perspective, that a future probe-based archival system might be expected to provide are shown in Figure 1. Technical challenges for probe-based storage in meeting such specifications are primarily concerned with three aspects: (i) storage capacity; (ii) write/read speeds; (iii) tip/media longevity. To provide the necessary capacity we need to be able to write and read over a relatively large (storage media) area at very high data densities in the region 1Tbit/sq.in to 10Tbit/sq.in. To provide the necessary write/read data rates we need to provide a high write/read speed per probe, typically 1 Mbit/s or more, and/or use large 2-D probe arrays. To provide the necessary longevity we must utilise storage materials with the necessary long-term stability and, importantly, mitigate any adverse effects of tip and media wear. We are addressing all these issues within the ProTeM project, via two alternative routes. The first uses thermo-mechanical probes and polymer media, as pioneered by IBM in their 'Millipede' system [1,2]. The second route utilises scanning electrical probes and electro-thermal write/read with phase-change media, and it is this approach that is the subject of this paper.

Although our primary objective is the research and development of the science and technology of small, low-power yet ultra-high capacity archival probe-storage systems, it is most likely that the solutions we develop will have significant applications in other important data storage sectors, in particular in the back-up sector. Archiving and back-up applications are often conflated, but are in fact two different forms of storage. A classic back-up application takes periodic copies (images) of active data in order to provide a method of recovering records that may be deleted or destroyed. Most backups are retained only for a few days or weeks as later backup images supercede previous versions. Thus, a backup is designed as a short-term 'insurance policy' to facilitate disaster recovery and has different read/write performance and data integrity/media longevity requirements. In particular the relatively high data rate required for back-up storage presents challenges in terms of implementation by probe storage techniques.

System Specifications		min	max	Units/comment
System Capacity		200	1000	TB
Transactions per day	read	2000	10000	per 24 hours
	write	1	10000	per 24 hours
streaming data rate	write	100	250	MB/sec
	read	100	1000	MB/sec
worst case access	write	1	10	secs
	read	1	10	
Typical file size for transfer		2KB	100MB	
Random access within one media unit			1	second
number of concurrent read users		10	1000	
number of concurrent write users		1	10	
Power consumption			300	watts
Spin-up" time			5	seconds

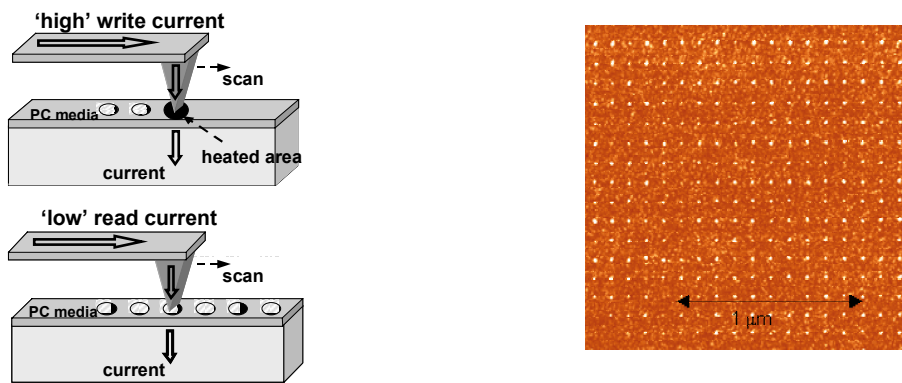
Media Level Specification		min	max	Units/comment
Media unit capacity		2	100	TB
Media read cycles	read	10 <sup>6</sup>		over media life
media life		20	50+	years (at 50C)
Sector size			8	k
RW cyclability		10,000		overwrites
Operating temperature range		-5	45	C

**FIG 1** Typical specifications, from a user-perspective, for a future archival probe-storage system

The ProTeM project involves ten technical partners drawn from the European industrial and academic sectors - IBM Research Zurich, FhG Itzenhoe, CEA-LETI Grenoble, Plasmon, Numonyx, Arithmatica, RWTH-Aachen, University of Twente and the University of Exeter.

## 2. PHASE-CHANGE PROBE STORAGE

The basic mechanism for probe storage using phase-change media is shown in Figure 2 and has been described in detail elsewhere [3-5]. Essentially the writing of bits involves an electro-thermal process in which Joule heating provides the energy required for crystallisation or amorphisation. The readout process is electrical and relies on sensing the large difference in electrical resistivity for the two phases. The configuration and write/read mechanism can be viewed as similar to that used in phase-change RAM devices, but in the case of probe storage the top electrode is the probe tip itself which moves in an x-y fashion to record the appropriate bit pattern (and of course the probes would be microfabricated into a large 2-D array in a practical system).



**FIG 2** Schematic of the electrical probe storage system using phase-change media, showing the recording and reading processes (left). Also shown (right) are experimentally achieved crystalline bits of approximately 20nm diameter written into an amorphous GeSbTe layer in a tri-layer stack (courtesy of S Gidon et al CEA-LETI Grenoble [3]).

Electrical probe recording with phase-change media has several attractive features not always present in other probe storage techniques. For example, since only the bit volume is heated during recording, the bit writing process consumes relatively low power. Also, the bit size is primarily determined by the tip electrical contact area, not the physical sharpness of the tip *per se*; thus it should be possible to design tips with small electrical contact radius but large physical contact radius and this might have beneficial effects in terms of reducing tip wear (a point to which we shall return later).

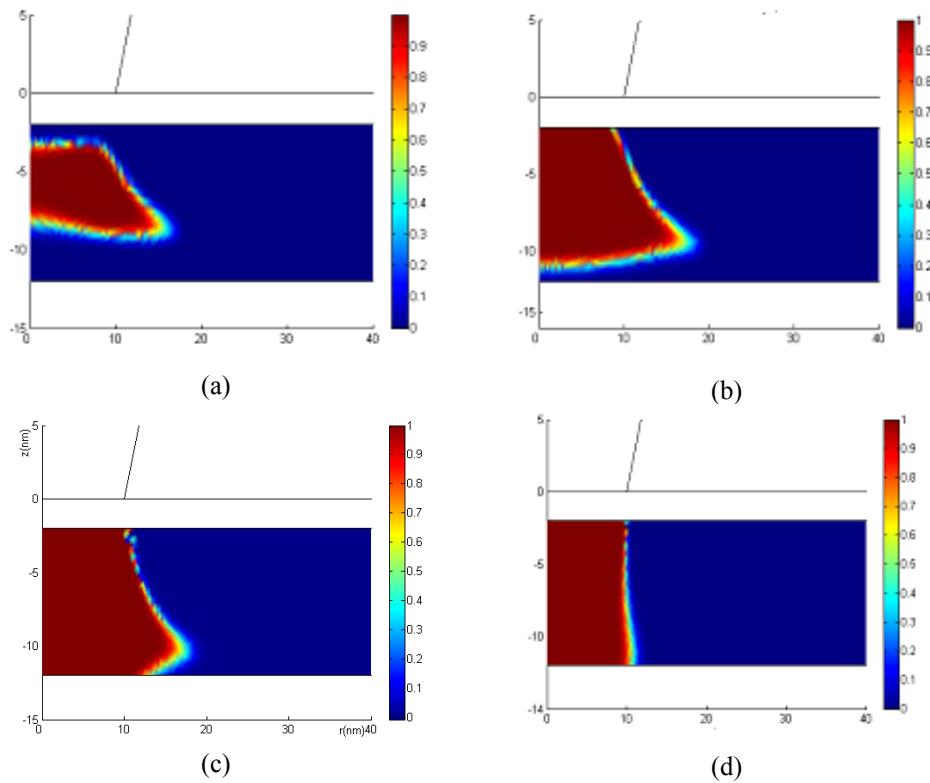
## 3. WORM MEDIA

Both WORM and RW media find applications in archival storage, and both media types are being developed in ProTeM. The basic WORM media format is shown in shown in Fig 3 and comprises a phase-change layer, in this case the 'standard'  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  alloy, with a conductive bottom electrode and a suitable capping layer. The capping layer provides passivation for the phase-change layer and reduces the effects of tip/media wear; in addition it modifies the electrical and thermal environment and strongly influences write/read performance. WORM functionality is provided by using an amorphous starting phase for the phase-change layer and by choosing appropriate electrical and thermal properties for the capping and electrode layers. By this approach crystalline bits may be written into the phase-change layer that are difficult to erase (i.e. re-amorphisation is inhibited).

WORM Stack	Material	Thickness (nm)	Resistivity (Ohm.cm)
Capping	Carbon	2-3	1 - 10
Phase-Change	$\text{Ge}_2\text{Sb}_2\text{Te}_5$	10-30	$0.1_{\text{crystalline}} - 1000_{\text{amorphous}}$
Bottom Electrode	Carbon	10	0.1 - 1
Si Substrate			

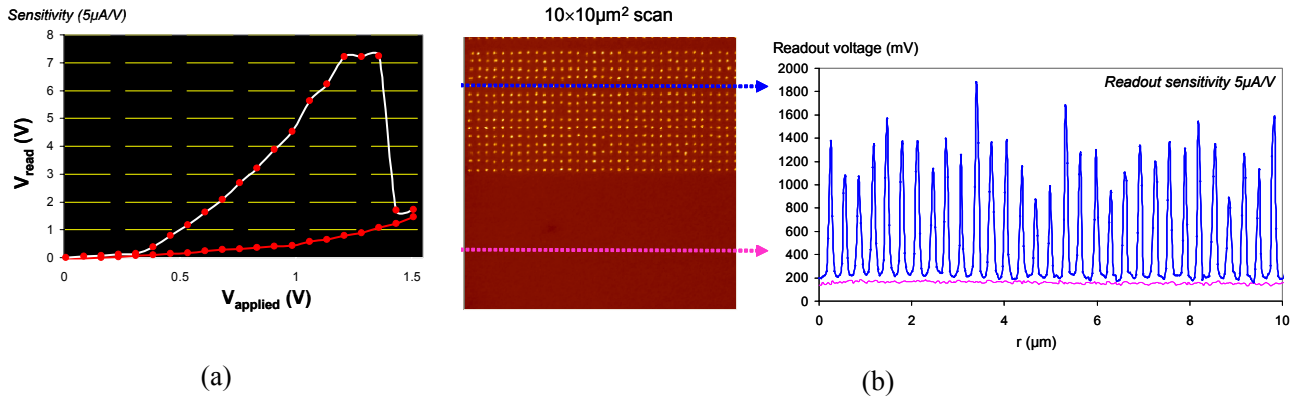
**FIG 3** The basic WORM stack (Si substrates with  $\text{SiO}_2$  layer on top are also used)

The write/read and erase performance of media stacks such as that shown in Fig 3 have been simulated using a numerical model described in detail in a previous work [5]. An interesting recent finding is that the capping/underlayer thermal conductivity plays an important role in determining the recorded bit shape. This is illustrated in Fig 4 where it is notable that the previously observed (in [5]) 'trapezoidal' embedded (in the centre of the phase-change layer) crystalline bit shape can be 'transformed', by reducing the thermal conductivity of the capping/underlayer, to a more desirable cylindrical shape extending through the whole thickness of the phase-change layer. In practice the thermal conductivity of thin carbon layers used here for capping and electrode layers is governed by the amount and structural disorder of the  $sp^3$  phase, and can vary quite dramatically over several orders of magnitude from around 0.1 W/mK to as high as 100 W/mK [7].



**FIG 4** Crystalline bits written into a 10nm thick GST layer with a 2nm thick capping layer and 10nm thick underlayer having electrical resistivities of  $2\Omega\text{cm}$  and  $1\Omega\text{cm}$  respectively and with thermal conductivities of (a) 10W/mK, (b) 5W/mK, (c) 2W/mK, (d) 0.2W/mK. A 100ns 10V tip-sample voltage pulse was applied in each case. The colour bar represents the fraction of crystalline material from zero (blue) to one (brown).

Preliminary experimental recording studies of WORM stacks similar in design to that of Fig 3 have been performed. Typical results are shown in Fig 5 where the characteristic I(V) curve for electrical switching of GeSbTe is observed. In this case the electrical switching appears at around 1.5V. The writing of crystalline bits was achieved by applying a tip-sample voltage pulse of 2.5V with pulse durations in the range 500ns to 10 $\mu$ s. Readout used a constant voltage of 0.4V and showed an average peak readout current of around 6 $\mu$ A for the crystalline bits compared to around 700nA for the amorphous background. The written bit sizes were relatively large (~80nm) in this case; this may have been because the tip used (a commercially available Pt/Cr coated conductive AFM tip) had a relatively large tip apex, but more likely was a result of a non-optimal value for the electrode layer electrical conductivity.

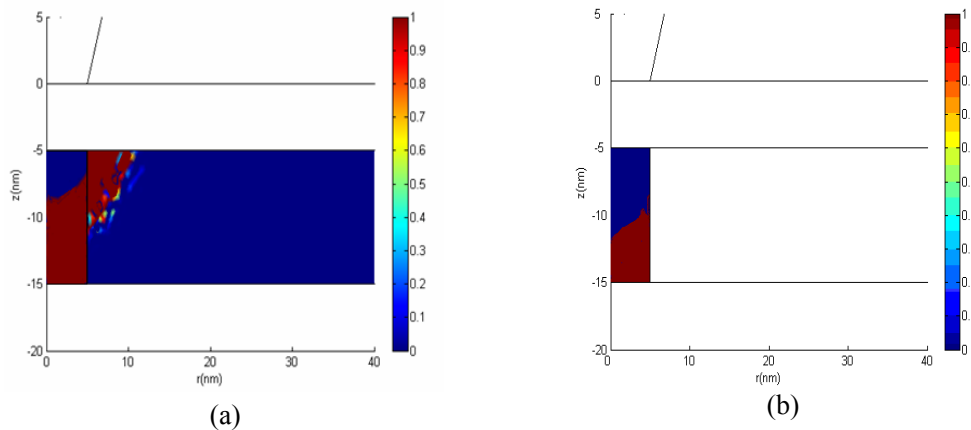


**FIG 5** Recording studies on Si/C(50nm)/Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>(10nm)/C(5nm) stack: (a) characteristic I(V) curve showing switching for a tip-sample voltage of around 1.5V in this case (the red dots and line correspond to the measurements during the voltage increase, the red dots and white line are obtained during the decrease of the applied voltage); (b) crystalline dots written with a 1 $\mu$ s 2.5V pulse (left) and readout signal for a constant readout voltage of 0.4V (right).

In addition to the use of carbon for the capping and electrode layers we are also investigating alternative materials. An obvious alternative electrode layer is TiN, since this has found widespread use as an electrode in phase-change RAM devices. Other alternatives include Mo, which is used in fourth generation solar cells based on CIGS (Copper Indium Gallium Arsenide) materials. For the capping layer we are studying the potential of CrSiO, which is often used as a thin film resistor because of the range of resistivity that can be achieved by varying the Cr: SiO ratio, and due to its low thermal coefficient of resistance. It may also be possible to use alternative materials for the storage layer itself. There are a number of WORM materials used for optical storage that may also be suitable for probe storage applications. Examples include TePdO material [8], Cu-alloy/Si films [9] and the so-called DD or "Dielectric Diluted" material (an alloy of Sb-Sn-In co-sputtered with the dielectric ZnS-SiO<sub>2</sub>) used for making archival data storage optical discs [10]. These, plus other alternatives, are all being investigated under the auspices of the ProTeM project.

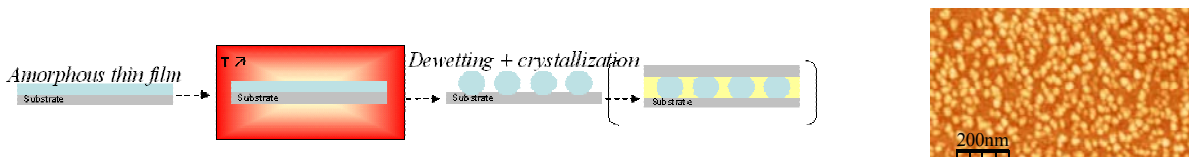
#### 4. RW MEDIA

To provide RW functionality written crystalline bits such as those shown in Fig 5 must be reamorphised. This requires heating of the bit volume to the melting temperature (around 900K for Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>) followed by a rapid cooling. A potential problem is that during such heating (and the subsequent cooling period), regions adjacent to the original bit experience temperature-time histories conducive to crystallisation. Thus, complete erasure may not occur; indeed, in some cases it may be that the original crystallised volume is increased rather than erased. This is illustrated in Fig 6a, where attempts to erase a previously written crystalline bit (cylindrical in shape and of diameter 10nm) has resulted in an amorphised region at the top of the layer but surrounded by a crystalline 'ring'. This crystalline ring is an ever-present feature of simulations so far carried out, and would result in a serious degradation of both readout SNR and achievable storage density. ProTeM is thus investigating three alternative methods that eliminate or reduce the effects of this ring formation, so providing RW performance. These approaches are (i) the use of patterned media, (ii) the use of slow-crystal-growth phase-change materials and (iii) the writing of amorphous bits in a crystalline background.



**FIG 6** Simulations of the erasure of a pre-written cylindrical crystalline bit of 10nm diameter: (a) the resulting crystalline fractions after the application of a 12V, 286ns erase pulse (with 100ns rising and 20ns falling edges); (b) the resulting crystalline fraction in a patterned 10nm diameter GeSbTe dot embedded in an SiO<sub>2</sub> matrix (for a 16V, 250ns erase pulse). Note that the blue region is fully amorphous and the media stack is as described in Fig 5.

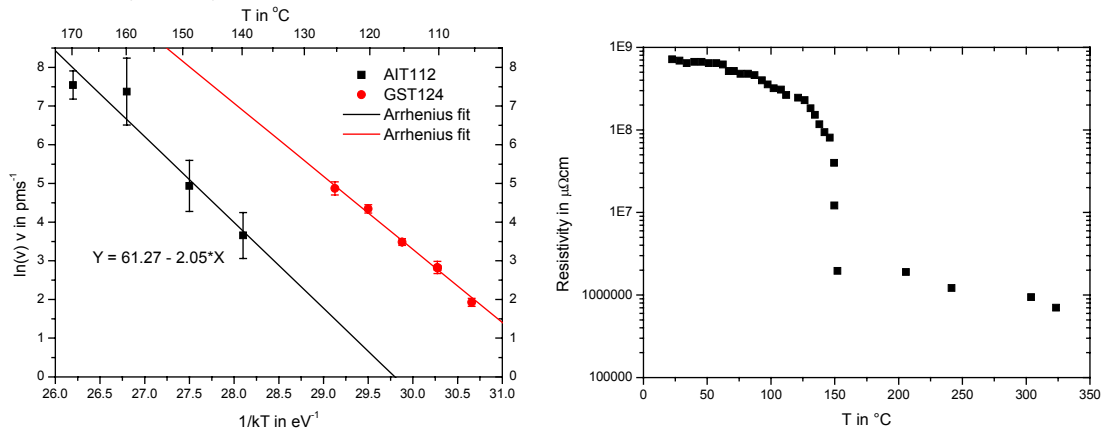
The use of patterned media is an obvious route to providing RW functionality, since in a sense it replicates the geometry of phase-change RAM devices, that have already been demonstrated to provide excellent RW performance. Indeed, both simulations (see Fig 6(b)) and experiment [11] of erasure and rewriting into patterned media using scanning probes have demonstrated that rewritability is feasible in such media. However, the patterning of phase-change materials at the small scales necessary to provide storage densities in the region of 1 to 10 Tbits/sq.in. is technologically difficult. It is likely that conventional lithography will prove prohibitively expensive. However, alternative routes such as nanoimprinting or self-assembly may be feasible in the future. In the ProTeM project we are investigating the self-assembly route for the production of nanoscale patterned phase-change materials. First investigations of self-organized phase-change nanostructures are based on a de-wetting processes of very thin films, the idea being to create nanoballs of phase-change materials from a continuous layer, as shown in Fig 7. Preliminary results have shown that, as would be expected, the substrate type and annealing conditions greatly affect the de-wetting process.



**FIG 7** Self-assembly of nanoscale phase-change dots by a de-wetting process showing the basic mechanism (left) and preliminary results for a 4nm GeSbTe film on a Si/ZnS-SiO<sub>2</sub> substrate (right - structures shown are ~ 3nm in height).

Even if it proves possible to fabricate nanoscale patterned media there is a concern that their use is incompatible with writing and reading by large 2-D arrays of probes, since the alignment of probe tips to patterned dots would be problematic using conventional lithographic techniques (assuming the tip array and patterned media are fabricated by separate lithographic processes), unless each tip has its own x-y actuation system, which would significantly increase the cost and complexity of array fabrication. In light of this a further alternative route to realising RW functionality to be investigated is the use continuous films of 'slow-growth' phase-change materials. The idea here is to prevent the formation of the crystalline 'ring-effect' by using a material whose crystal growth rate is too slow to allow for crystallisation to occur during the erase pulse (and subsequent cooling period). Simple calculations suggest that the crystallisation speed should be lower than  $0.1\text{ms}^{-1}$  (at  $400^{\circ}\text{C}$ ) to enable successful reamorphisation. So far we have identified the tetrahedral semiconductor AgInTe<sub>2</sub> as a very promising candidate for RW applications. It shows a very slow crystallisation process, and has a suitable electrical contrast between amorphous and crystal phases (see Fig 8).

We have also identified  $\text{GeTe}_6$  as a good candidate, based on the knowledge that it is a good glassformer and so should crystallise very slowly.



**FIG 8** (Left) Arrhenius plot of  $\text{AgInTe}_2$  compared to  $\text{GeSb}_2\text{Te}_4$ . It can be seen that for the same temperatures the growth velocity of  $\text{AgInTe}_2$  is smaller. (Right) Temperature dependent resistivity measurement on  $\text{AgInTe}_2$  (from Detemple et al, APL 83:2572, 2003).

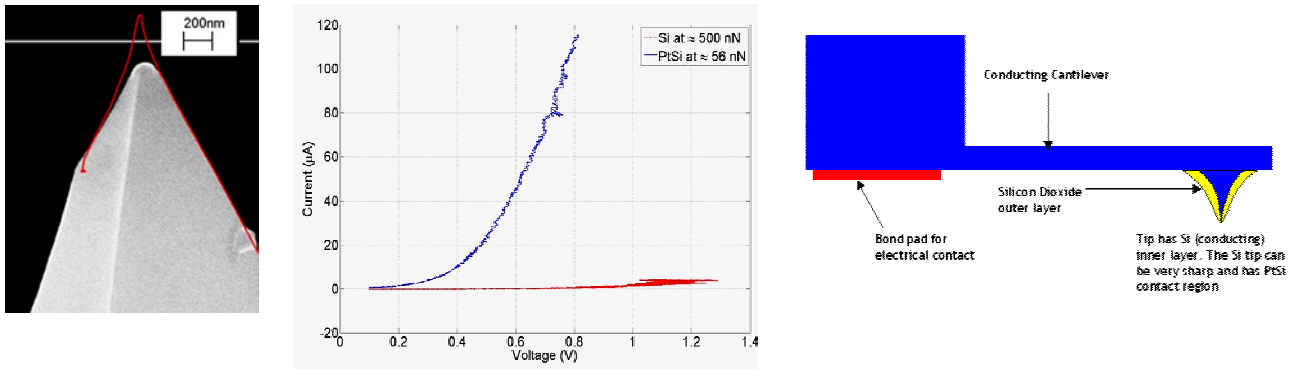
The final approach to be investigated to provide RW functionality is the use of a crystalline starting phase in which amorphous bits are recorded and then erased by re-crystallisation. This is the approach used in commercial phase-change based RW optical disks. ProTeM partners are currently investigating the feasibility of this approach and results will be presented in subsequent publications.

## 5 PROBE DESIGN

The final aspect we will consider in this paper is that of the design and fabrication of the probe itself. While the design of thermo-mechanical probes is more complex than that of electrical probes, and their fabrication costs relatively high, these disadvantages have been offset thus far by the fact that electrical probes exhibit a high rate of tip wear in phase-change media-based probe storage. In Fig 9(a) for example we show a commercial PtIr coated tip after just 25mm of sliding. The wear is exceptionally high (of the order  $10^6 \text{ nm}^3/\text{m}$ ) at the loading forces (typically 100nN or higher) required for reliable conduction. The rate of wear of bare silicon tips is also relatively high, being around  $7000 \text{ nm}^3/\text{m}$  on carbon in ambient conditions. Both the high wear rates and the relatively poor contact quality associated with high wear can result in complete loss of functionality of a probe storage device. Thus we have focused our probe design efforts for phase-change applications towards improving both wear resistance and contact reliability by using alternative tip materials. In particular platinum silicide offers the potential for superior wear resistance as well as improved conduction. We have fabricated cantilevers with PtSi tip apexes, and our experiments show that the estimated wear rate of PtSi on carbon in ambient conditions is only  $175 \text{ nm}^3/\text{m}$ , much less than silicon on the same medium. Thus by using PtSi tips we have reduced tip wear to a value that is 30 times less than with standard silicon tips, and is several orders of magnitude smaller than commercial PtIr tips. The PtSi tips also help in dramatically improving the conduction reliability of the tips, greatly reducing the contact resistance compared to silicon tips, as shown in Figure 9(b). We have shown that currents of  $800 \mu\text{A}$  can be sustained through these tips without causing catastrophic damage to their apexes - this is several orders of magnitude greater than for commercial PtIr coated tips of similar tip apex radius ( $<20 \text{ nm}$ ). Details on the wear experiments on these tips and comparisons vis-à-vis silicon tips are discussed in [12].

While PtSi tips show a dramatic improvement in wear resistance and superior conduction as compared to both commercial and silicon tips, having a tip with negligible amount of wear would be ideal. In this respect the fact that, as pointed out in §2, for electrical probe storage the resolution is not a function of the physical sharpness of the tip but a function primarily of the electrical contact area, provides an opportunity for innovative tip design that promises to meet both resolution and wear requirements. Such a design is shown in Fig 9(c); here a very small, highly conducting,

wear-resistant PtSi region is encapsulated into a tip with a much larger physical contact radius determined by an Si/SiO<sub>2</sub> cladding layer. We have fabricated such tips, and in future we shall evaluate the long-term reliability/ endurance of these tips and their performance while writing and reading over large sliding distances.



**FIG 9** (a) Wear of commercial PtIr coated tip after 25mm of contact sliding; (b) conduction of Si and PtSi tips on Au; (c) the concept of the encapsulated electrical tip

## 6 CONCLUSIONS

We have reported on recent phase-change research from the EU FP6 project ProTeM (Probe-based Terabit per square inch Memory) that aims to develop scanning-probe based storage media and systems suited to archival and back-up storage applications, with storage densities in the range 1 to 10Tbits/sq.in. We have demonstrated WORM functionality in tri-layer media stacks based on GeSbTe with carbon capping (passivation) and electrode layers. Alternative alloys and techniques more suited to RW applications are also under investigation and have been discussed. A novel form of encapsulated electrical tip that allows for high resolution write and read while at the same time dramatically reducing the effects of tip wear has also been demonstrated.

## Acknowledgements

We gratefully acknowledge the European Commission for financial support for the ProTeM project via its FP6 programme. A full list of ProTeM project partners can be found at [www.protem-fp6.org](http://www.protem-fp6.org)

## REFERENCES

1. P. Vettiger et al 'The Millipede - nanotechnology entering data storage', *IEEE Trans Nano*, **1**, 39 (2002)
2. H Pozidis et al, 'Demonstration of thermomechanical recording at 641 Gbits/in<sup>2</sup>', *IEEE Trans Magn*, **40**, 2531 (2004)
3. S Gidon et al, 'Electrical probe storage using Joule heating in phase-change media', *Appl. Phys. Lett.*, **85**, 6392 (2004).
4. H Satoh, K Sugawara and K Tanaka, 'Nanoscale phase-changes in crystalline GeSbTe films using scanning probe microscopes', *J Appl Phys*, **99**, 024306 (2006)
5. C D Wright, M Armand and M M Aziz, 'Terabit per square inch data storage using phase-change media and scanning electrical nanoprobles', *IEEE Trans Nano*, **5**, 50 (2006)
6. K Tanaka et al, 'Scanning nonlinear dielectric microscopy nanoscience and technology for next generation high density ferroelectric storage', *Jpn J Appl Phys*, **47**, 3311 (2008)
7. M Shamsa et al, 'Thermal conductivity of diamond-like carbon films', *Appl. Phys. Lett.*, **89**, 161921 (2006)
8. H. Kitaura, K. Hisada, K. Narumi, K. Nishiuchi and N. Yamada, 'Multi-layer write once media with Te-O-Pd films utilizing a violet laser', *Proc of SPIE*, **4342**, 340 (2002)
9. H Inoue et al, 'Inorganic write-once disc for high speed recording' *Jpn. J. Appl. Phys.*, **42** (1,2B), 1059 (2002)
10. C E Davies, 'Key technology for Ultra Density Optical', *E\*PCOS03* ([www.epcos.org](http://www.epcos.org))
11. H J Kim et al, 'Structural phase transitions of GeSbTe cells with TiN electrodes using homemade W heater tip', *Appl. Phys. Lett.*, **90**, 083103 (2007).
12. H Bhaskaran, A. Sebastian and M Despont, 'Nanoscale PtSi tips for conducting probe technologies', *IEEE Trans Nano*, in press (2008).