Phase-change technologies: from PCRAM to probe-storage to processors

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ABSTRACT

Phase-change materials based on chalcogenide alloys, for example GeSbTe and AgInSbTe, show remarkable properties such as: the ability to be crystallized by pulses in the (hundreds of) femtoseconds region while at the same time withstanding spontaneous crystallization for many years; the ability to be cycled between phases 10^{12} times or more; the existence of a huge contrast between the refractive index of the phases; the existence of a huge electrical contrast between phases. These remarkable properties make phase-change materials suitable for a wide range of optical and electrical applications, for optical and electrical memories, for optical routers, for optical and electrical processors. In this paper we describe theoretical and experimental investigations of some of the key application areas, with a view to providing insights into the possible future use of phase-change materials.

Key words: phase-change technologies, phase-change memories, phase-change processors, femtosecond switching

1. INTRODUCTION

Over the past twenty years and more there has been great interest in chalcogenide materials, such as GeSbTe or AgInSbTe alloys, for a range of data storage applications. Currently the most prominent and widespread use of such materials is in the re-writeable phase-change optical memory disks, such as CD-RW, DVD +/- RW and re-writeable Blu-Ray formats etc. Their use in non-volatile, solid-state, electrical memories - the so-called PCRAM - first investigated nearly forty years ago, is also currently of much interest, as they offer a possible replacement for the conventional silicon-based flash memory currently used in USB memory sticks and other memory card formats. PCRAM offers excellent scalability, good endurance (cyclability), fast write/read speeds and the potential for multi-bit storage. Furthermore, the PCRAM memory can operate as a true random-access device, meaning that individual cells can be written, erased and re-written, unlike in conventional CMOS flash memory architectures. Such capabilities have been exploited in the first commercial application of PCRAMs - a 60-nm node 512-Mbit PCRAM device with an eraze time approximately ten times faster than (NOR-type) flash memory [1].

The use of phase-change materials beyond the 'conventional' realms of optical and solid-state electrical memories is also of much current research interest. For example, scanning-probe-based storage using phase-change media is also possible, with the potential for multi-Terabit per square inch storage densities having been demonstrated [2]. There is also the possibility of using phase-change materials to provide switchable optical routers for telecommunications applications, and for the fabrication of photonic crystals [3]. More remarkable and far-reaching potential applications of phase-change technology, recently discussed by S.R. Ovshinsky and co-workers, is the possible use of phase-change materials for electrical and/or optical processing in a non-Von-Neumann type architecture in which storage and computation are performed by the same phase-change 'cell' [4,5]. Furthermore, such phase-change processors might also possess the ability to carry out a form of 'cognitive processing', somewhat analogous to the operation of a brain neuron.

All of these current-day and potential future applications of phase-change materials rely on a reversible phase transformation of the chalcogenide alloy between the amorphous and (poly)crystalline states. In optical disk memories such phase-transformations are brought about by heating with a focused laser; readout relies on the different optical reflectivities of the two phases. In electrical phase-change memories, data is written or erased by resistive heating caused by a pulse of electrical current injected into the phase-change layer; readout relying on sensing the

different electrical resistivities of the two phases (that can differ by more than a factor of a thousand). Thus, it is clear that phase-change materials have many technologically important applications, and, to aid in the future design and development of new and improved devices and applications, it is necessary and desirable to have a thorough understanding of the phase-transformation processes that make these materials so useful. In this paper therefore we describe various theoretical and experimental approaches that we currently use to help understand the phase-switching mechanism in chalcogenide alloys, and describe the influence of such switching characteristics on the likely performance attributes of a number of specific applications, including PCRAM, scanning-probe memories and phase-change processors.
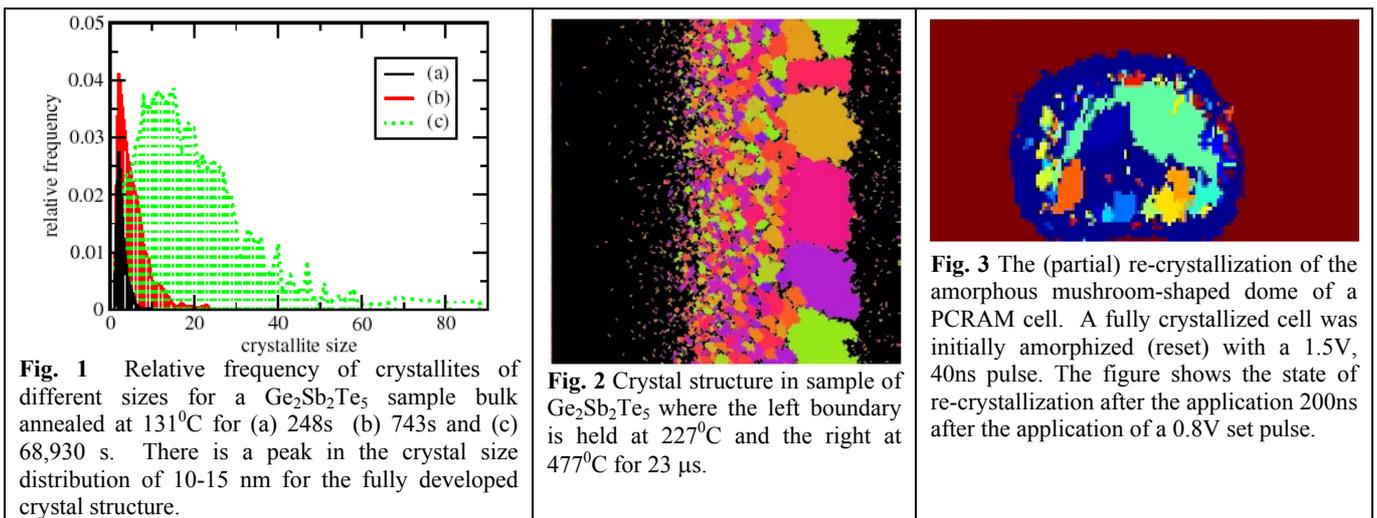
2. PCRAM MODELLING

As mentioned above, the commercial use of phase-change RAM devices has already started. However, to compete effectively in mainstream mass-storage applications, where CMOS (NAND-type) flash memory and magnetic hard disk technologies currently dominate, it will be necessary to increase significantly the storage density currently achieved with PCRAM. The main routes to achieve this are: (i) by direct downscaling (i.e. moving to smaller technology nodes) of single bit cells; (ii) by vertical stacking (i.e. 3D device architectures) of single bit cells; and (iii) by the implementation of multi-bit cells. While progress via route (i) is expected as a matter of course, such progress is relatively slow and costly, and to date phase change technology lags somewhat behind conventional CMOS-flash memory technologies (already at or below the 30nm node). Progress via route (ii) potentially requires complex 3D device fabrication techniques, although significant advances have been made recently by the integration of phase-change cells and selector devices in a relatively simple stackable cross-bar architecture [6]. Increasing PCRAM storage capacity by route (iii), the use of a multilevel cell (MLC) approach, is, on the face of it, a simple and attractive proposition, and could find applications not only in mass storage (flash replacement) but also, as recently suggested, as a replacement for conventional DRAM [7,8]. Whichever route, or routes, prove the most viable for future PCRAM development, understanding and modelling of the crystallization processes on the nanoscale will be most important.

Several methods have been used over the years to model the process of crystallization in phase-change alloys, such as the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model. Unfortunately many of the assumptions on which JMAK formalism is based are violated in real switching events in phase-change devices. Furthermore JMAK cannot distinguish materials with the same crystallized fraction but different crystallite size distributions, and this is important to predict the dynamical progress of the complex annealings often necessary for memory applications. Another common modeling approach is based on separable nucleation and growth models, often used to examine optical phase-change recording. However, such approaches deal only with crystal clusters at or above the critical stable size, whereas sub-critical clusters are also likely to play a significant role in the nanoscale dynamic behaviour of future devices. An attractive, physically plausible, alternative to these more established methods is the rate-equation approach that models the evolution of the crystal cluster size distribution during the entire phase-transformation process. Using rate equations, the frequencies of attachment and detachment of material "monomers" representing unit changes in crystal cluster sizes can be determined. We have investigated the use of both discrete and continuous versions of the rate-equation approach to model phase transformations in $Ge_2Sb_2Te_5$, and they have proved extremely useful in predicting bulk annealing behaviour [9, 10]. However, the rate-equation approach is computationally intensive and not directly suited to cases, such as optical and electrical memories, where understanding the spatial distribution of crystallization is important. More recently, *ab initio* atomic-scale models of crystallization processes in phase-change materials have been developed based on the well-known density function theory (DFT) approach [11, 12]. However, DFT-type approaches come at a steep computational price, and only arrangements of a few tens of atoms can be simulated without supercomputing resources, making such approaches unsuited to understanding and predicting the details of real device operation and for use in real device design. We have therefore developed a new approach that is potentially capable of spanning the scales between atomistic methods, such as DFT, and bulk-scale methods, such the JMAK formalism. The model combines the attractive thermodynamic features of the rate-equation approach with elements from probabilistic cellular automata models and phase-field models. In addition, it uses the Gillespie algorithm for time stepping, so providing for fast simulation of complex spatial and temporal heating/cooling cycles essential to the operation of current and future phase-change memory devices. A high level of simplicity is maintained by using a discrete time and lattice space model, while retaining thermodynamic realism and

hence keeping fitting parameters to a minimum. Only a two dimensional 2D version of the model is presented here, but the extension to 3D is, in principle, computationally trivial. The material space to be modelled is thus described as a 2D lattice of discrete grid points, where each site is either crystalline or amorphous and there is an underlying orientation that varies continuously; these sites are on the length scale of monomers (the basic building block for the crystal structure). Crystallization can be thought of as a two-stage process; nucleation where a small crystallite needs to overcome an energy barrier dominated by interfacial energy, and growth where the crystallite grows according to the availability of neighbouring monomers and dominated by bulk energy. Each site is assumed to have a set of locally determined rate constants for transitions into a new state. These rates depend only on the current state of the site and that of its immediate neighbours. For the rates of growth and dissociation for modeling of GST materials, thermodynamic parameters from previous work are used [9, 10, 13, 14]. The Gillespie algorithm [15] can be used to simulate the evolution under the assumption that the events are independent, instantaneous, and never simultaneous.

Full details of the Gillespie-type Cellular Automata (GCA) algorithm are given in our previous work [14] and in a companion EPCOS paper [16]. Here we present some specimen results that demonstrate some of the attractive features of the GCA approach. In Fig. 1, for example, we show how the distribution of crystallite sizes changes during a typical bulk annealing of $Ge_2Sb_2Te_5$. Note in particular that, in this case, there is a peak in the crystal size distribution of 10-15 nm for the fully developed crystal structure. In Fig. 2 we show the simulated crystal structure formed in a $Ge_2Sb_2Te_5$ sample with one boundary held at 227^0C and the other at 477^0C for 23 μs. On the left hand side the growth is very slow while on the right side there is rapid dissociation, so a band of crystallites forms towards the middle of the sample, with a range of temperature-dependent sizes and (depcited by the different colours) a variety of preferred orientations. As a final example of the GCA method we show in Fig. 3 the crytallisation state of a PCRAM cell after the application of a 200 ns, 0.8V set pulse.

Fig. 1 Relative frequency of crystallites of different sizes for a $Ge_2Sb_2Te_5$ sample bulk annealed at 131^0C for (a) 248s (b) 743s and (c) 68,930 s. There is a peak in the crystal size distribution of 10-15 nm for the fully developed crystal structure.

Fig. 2 Crystal structure in sample of $Ge_2Sb_2Te_5$ where the left boundary is held at 227^0C and the right at 477^0C for 23 μs.

Fig. 3 The (partial) re-crystallization of the amorphous mushroom-shaped dome of a PCRAM cell. A fully crystallized cell was initially amorphized (reset) with a 1.5V, 40ns pulse. The figure shows the state of re-crystallization after the application 200ns after the application of a 0.8V set pulse.

3. SCANNED-PROBE STORAGE

The basic mechanism for probe storage using phase-change media has been described in detail elsewhere [17] and a typical storage architecture is shown in Fig. 4. The basic structure comprises a phase-change layer sandwiched between two electrodes, in this case a TiN bottom electrode and a top electrode comprising a conductive scanning probe microscopy type tip (in this case a PtSi tip that has been shown to have far superior conduction and wear properties as compared to standard coated conductive AFM type tips [18]). The similarity between the probe architecture of Fig. 4 and the archetypal 'pillar-type' PCRAM memory cell is clear, with the heating pillar of the PCRAM cell replaced in the probe storage case by the probe tip. However, a major difference between PCRAM and probe storage memories is that in the latter the probe tip is physically moved (scanned in x and y) to write and read bits in the phase-change layer. This means that a protective capping layer must be used that can protect the phase-
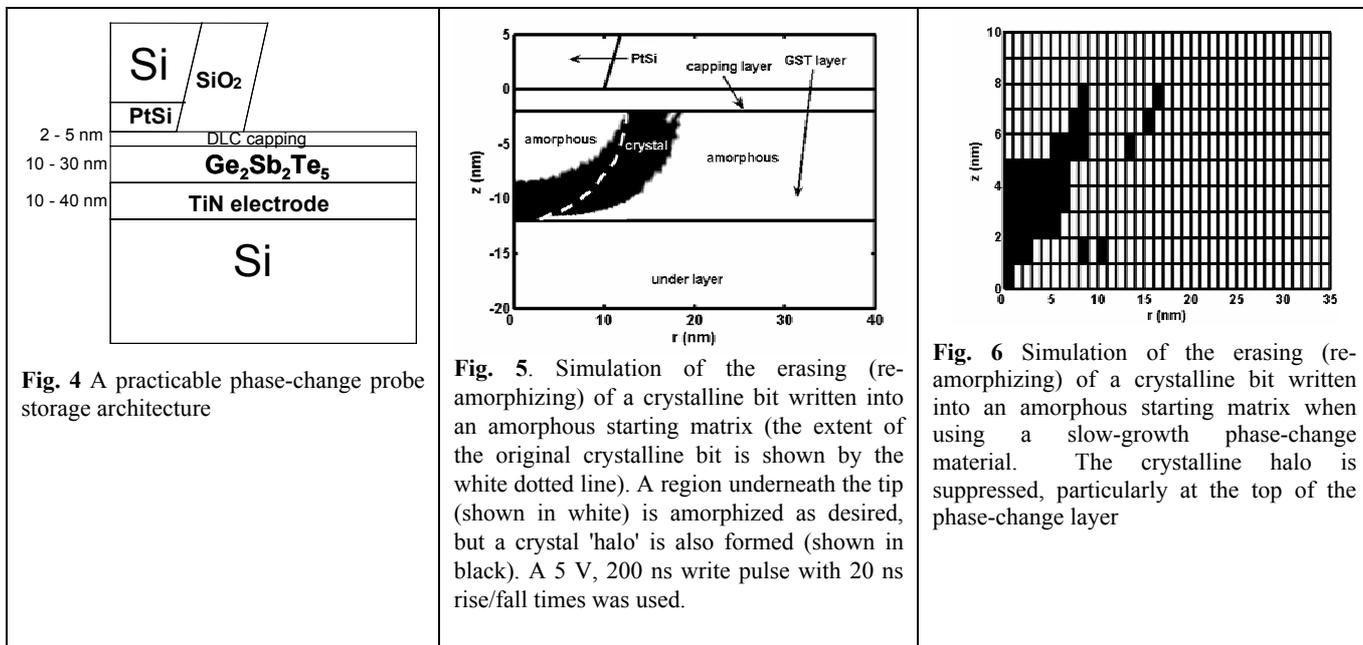
change layer from oxidation, while at the same time providing good tribological properties to allow the tip to move smoothly over the medium surface and protecting against scan induced wear (of both the tip and the medium). The capping layer must also be electrically conducting with a resistivity high enough to allow for effective writing and reading, but low enough so that it does not act as a shorting path for current from the tip. It should also have a relatively modest thermal conductivity, to help retain heat inside the medium structure so allowing crystallization and amorphization temperatures to be reached with realistic tip-sample voltages. Suitable electrical and thermal conductivities can be found in diamond like carbon (DLC) films that can also be deposited into very thin and smooth layers and exhibit very good tribological properties [19]. DLC films also possess good relatively good thermal stability - this is important because the capping layer can reach high temperatures, particularly during the writing of an amorphous mark. We have previously reported on the design of phase-change probe storage media and systems for use primarily in WORM (write-once-read-many) applications, such as for archival storage [20]. It is also interesting to investigate the design of a re-writeable phase-change probe storage format. As we know, phase-change alloys such as $Ge_2Sb_2Te_5$ can be cycled between amorphous and crystal phases innumerable times, and so the design of a re-writeable probe storage format might at first seem relatively straightforward.

In 'conventional' phase-change memories, including phase-change optical disks and PCRAM devices, re-writeability is implemented using a crystalline starting phase into which an amorphous bit is recorded and subsequently erased (re-written) by re-crystallization (as in Fig. 3 above). Thus it might seem that using a similar approach for probe storage, i.e. having a crystalline starting phase into which an amorphous bit is written by the probe tip and subsequently erased (re-written) by re-crystallization, should be feasible. However, the actual writing of amorphous bits in an initially crystalline phase by a scanning electrical probe has proved to be problematic, at least in practicable media, whereas there are numerous reports of the successful writing of crystalline bits in an amorphous matrix (eg [21-22]). Indeed, the writing of amorphous bits in phase-change media using electrical probe techniques has, to our knowledge, only been demonstrated experimentally by one group [23] and in that case the phase-change storage medium was contacted directly by the writing tip while the phase-change layer itself was protected from oxidation by being immersed in an inert liquid. However, such a liquid protective layer is not practicable for real storage systems. In light of the apparent difficulties in writing amorphous marks in practicable phase-change media stacks using scanning conductive probes, we have therefore investigated a number of alternative approaches to providing re-writeability when starting in the amorphous phase (i.e. writing crystalline marks and erasing by re-amorphization). However, a particular problem when trying to erase crystalline marks in an amorphous matrix is the formation of a crystalline 'halo' around the erased (re-amorphized region), as illustrated in Fig. 5. Such 'halo' effects have been observed experimentally in laser bit writing studies on similar materials and are an ever-present feature so far in our simulations of the erasure of crystalline bits in probe storage systems. It should be pointed out that the 'halo' effect would result in a serious degradation of both the readout signal and the achievable storage density. It might be tempting to use a higher amplitude erase pulse to try and increase the effectiveness of the erase (amorphization) process. However, as might be expected, this does not remove the crystallization 'halo', but simply shifts it laterally. Decreasing the fall time of the erase pulse also does not remove the 'halo' effect. Clearly an alternative approach to eliminate or suppress the crystal 'halo' effect is needed. We have studied two such possible methods, namely (i) the use of patterned media and (ii) the use of a phase-change layer made from a slow crystal growth material.

Suppression of the formation of the crystal 'halo' effect should be relatively straightforward using a patterned medium in which small phase-change regions are isolated from each other, preferably by some kind of thermal insulator. This removes phase-change material from the region in which the crystalline halo would like to form. As might be expected, simulations indicate that the writing, erasing and re-writing of crystalline marks in such patterned media should be possible (see [24] for details). However, the use of patterned media with scanned probe storage is problematic for two main reasons. Firstly the patterning of media at the dimensions required for ultra-high density storage requires expensive state-of-the-art lithography, a technique not readily suited to the provision of relatively cheap mass storage media. Secondly, (and even if lithography at the nanoscale were to become much simpler and cheaper), there remains a fundamental problem with the use of patterned media in probe storage systems, a problem not often mentioned in the literature. For probe storage to be a viable technology requires the use of 2D probe arrays, with large numbers of probes within such arrays operating in parallel in order to provide sufficient write/read data

rates. Each individual tip within such an array thus addresses its own data field, typically an area around 100 μm x 100 μm. For tips to operate in parallel, they must each be properly and simultaneously located over the bits in their own fields. This is likely to be a major problem in patterned media, assuming 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. Thus the viable use of patterned media with probe arrays seems problematic at present.

Due to these potential problems with patterned media, we have investigated an alternative route to realise the erasing of crystalline bits, namely the use of 'slow-growth' phase-change materials. Traditionally, at least in the case of optical storage, faster and faster crystallization materials have been sought to allow for faster and faster data rates. However, in probe storage systems the overall data rate is governed not only by the data rate per tip, but also by the number of tips operating in parallel in the 2D tip array. Thus, the data rate per tip can be relatively modest so that having a phase-change material with a very fast crystallization speed is not really necessary. Therefore, it might be possible to prevent the formation of the crystalline 'halo' by using a material whose crystallization rate is too slow for crystallization to occur during an eraze pulse. Indeed, we have found that for a material with a maximum growth velocity of 0.1 ms^{-1} the formation of a crystalline halo is indeed suppressed, as shown in Fig. 6. A search for a suitable slow-growth material has been made and, as described in our EPCOS 2008 paper [20], $GeTe_6$ seems to 'fit the bill'.

Fig. 4 A practicable phase-change probe storage architecture

Fig. 5. Simulation of the erasing (re-amorphizing) of a crystalline bit written into an amorphous starting matrix (the extent of the original crystalline bit is shown by the white dotted line). A region underneath the tip (shown in white) is amorphized as desired, but a crystal 'halo' is also formed (shown in black). A 5 V, 200 ns write pulse with 20 ns rise/fall times was used.

Fig. 6 Simulation of the erasing (re-amorphizing) of a crystalline bit written into an amorphous starting matrix when using a slow-growth phase-change material. The crystalline halo is suppressed, particularly at the top of the phase-change layer

4. PHASE-CHANGE PROCESSORS

As mentioned in §1, Stanford Ovshinsky has postulated on the use of phase-change materials for the provision of not only memory, but also for general-purpose computation and even cognitive-type processing [4,5]. In Ovshinsky's approach both the processing and the storage of information can be carried out by the same phase-change 'cell', so providing an exciting and new non-Von-Neumann type processing architecture. The origins of such possibilities lie in the detail of the phase-transformation event itself. In conventional (electrical) phase-change memories crystallization relies on both electronic and thermal effects; applying a voltage above a certain value induces a conducting on-state in the previously high-resistance amorphous material, allowing current to flow which in turn generates heat to drive crystallization. The electrical resistance during switching changes abruptly at the 'percolation threshold', where growing (nano)cystallites merge to form the first conducting pathways between device electrodes. It is the pre-

threshold region that offers the potential to perform general-purpose computation and provide artificial neuron-like capabilities. This may be explained by considering pre-percolation behaviour to involve energy-accumulation; energy is accumulated and crystal clusters grow as each input pulse is applied and when enough energy has been accumulated to reach the percolation threshold the cell resistance changes abruptly. This energy accumulation property has the potential to implement basic mathematical operations such as addition, subtraction, multiplication and division, as well as more complex functions such as factoring, encryption and logic [5]. The accumulation property, the presence of a distinct threshold, and a non-linear (output) transition (between resistance states) mimic the basic action of a biological neuron. Furthermore, the (synaptic) weighting of inputs might be provided by another phase-change cell operating in the multi-level storage regime. Thus, an artificial neuron might be achieved using only phase-change cells, operating in the energy-accumulating regime to mimic the operation of the neuronal body and the multi-level storage regime to mimic synaptic weighting. Although the energy accumulation regime and processing is described above in terms of electrical excitation of phase-change materials, it is also applicable to optical excitation. Indeed, it would be possible to combine the electrical and optical domains, for example by applying the excitation pulses optically, but detecting the threshold switching events electrically.

The energy accumulation property that forms the basis of using phase-change materials to provide processing functions has been demonstrated by S. R. Ovshinsky and co-workers for both electrical [5] and optical configurations [4]. We have previously investigated the energy accumulation property theoretically, using a rate-equation model to calculate the fraction of crystallized material in a phase-change 'cell' when subject to various excitation pulses [13]. A typical result from such simulations is shown in Fig. 7. Here an initially amorphous cell (all monomers) was subject to nine successive 50 ns, 350^0C annealing pulses, 1μs apart. The cell was then reset into the amorphous state. In reality voltage or current pulses would be applied to the phase-change cell and heating would be due to a combination of electrical and thermal effects, but the origin of the heating is not considered here, merely its effects on crystallization behaviour. Figure 7 reveals a monotonically increasing crystallized fraction with increasing number of anneal pulses. The number of monomers (not shown) decreases monotonically while the number of dimers (n=2) and multimers (n = n_{max}) increases monotonically through the anneal. The phase-change cell is effectively accumulating energy with each pulse and crystal clusters grow in size and number as the anneal progresses. Each particular crystallized fraction in the annealing cycle corresponds to a particular cell resistance in a real device and so by monitoring the cell resistance a decimal counter/adder could easily be obtained. Indeed, to make the process of decimal addition even simpler the device could be operated in threshold mode, where the completion of a count to ten is designed to coincide with crossing the percolation threshold. For spherical clusters the percolation threshold occurs theoretically at a 1/3 crystal fraction. It would be a simple matter to change the annealing regime for the percolation threshold to be reached after ten pulses.

We have also investigated the potential for performing processing functions with phase-change materials in the femtosecond optical regime. The ability to perform high-level arithmetic and/or logical processing on the femtosecond time scale, coupled with the ability to store the outputs of the processing in the same 'cell' that performs the processing would be an exciting achievement. To carry out such experiments we used the Ti-sapphire based optical pump-probe laser system shown in Fig. 8. The arrangement includes a pulsed pump beam and a CW probe beam that are overlapped on the sample surface within the focal plane of an optical microscope. The pulsed beam is used to excite the phase-change material (here a $Si/ZnS-SiO_2/Ge_2Sb_2Te_5/ ZnS-SiO_2$ film) while the probe beam measures the reflectivity of the pulsed region. Typical results are shown in Fig. 9 for 70 fs, 0.2μJ pulse excitation. It can be seen that the sample remains in the pre-switching 'energy accumulation' mode until around 250 pulses are received in this case. In this arrangement the system could be used to perform arithmetic computations to the base 250. Alternatively excitation pulses might be combined to reduce the base to a more suitable value, e.g. if a single excitation consists of 25 pulses, the threshold for switching would be reached after 10 pulses. It should also be possible to reduce the number of individual pulses required to reach the threshold by changing the pulse energy and/or duration - Fig. 10 shows the results of theoretical calculations of the effect of 70 fs pulses of different energies on the switching threshold which seems to confirm this view.
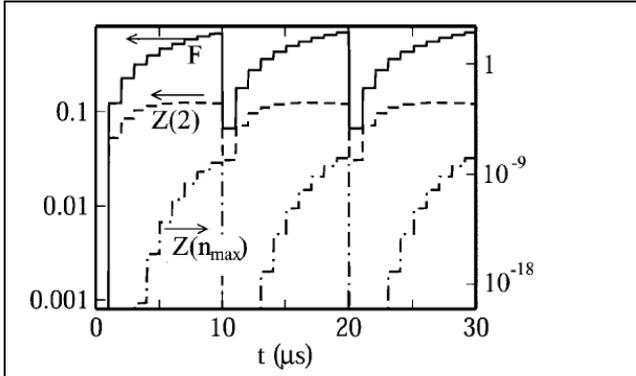
Fig. 7 Simulated fraction of crystallized material (F) and concentration of dimers (Z(2)) and multimers ($Z(n_{max})$) for a series of nine 350^0C, 50 ns excitation pulses. The phase-change cell accumulates energy and crystal fraction with each pulse and re-amorphized after the ninth pulse.
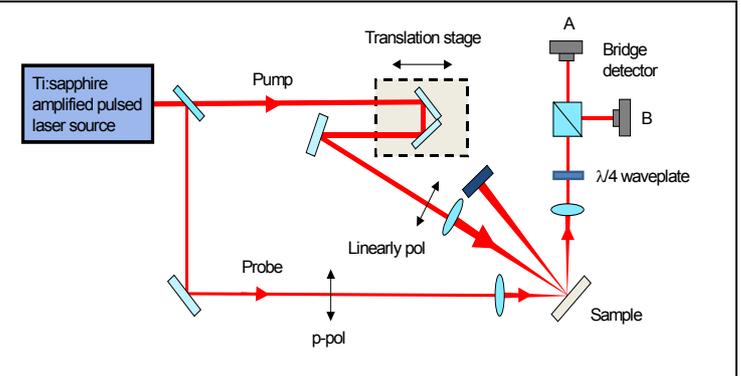

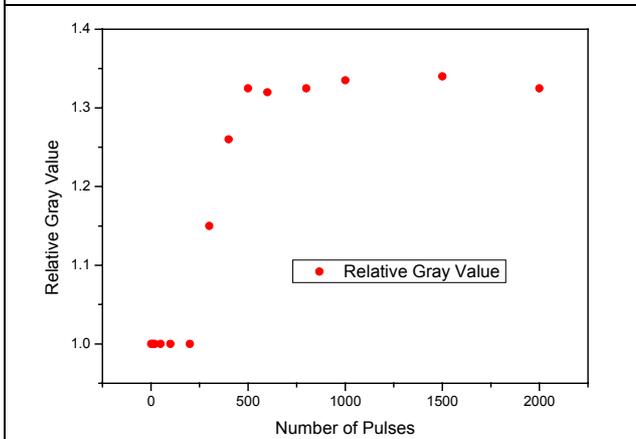**Fig. 8** Time-resolved laser set-up for femtosecond crystallization and amorphization experiments

Fig. 9 Experimental results for crystallization of $Ge_2Sb_2Te_5$ optical disk sample using multiple 0.2μJ femtosecond pulses. The sample remains in the pre-switching 'energy accumulation' mode until around 250 pulses are received in this case.
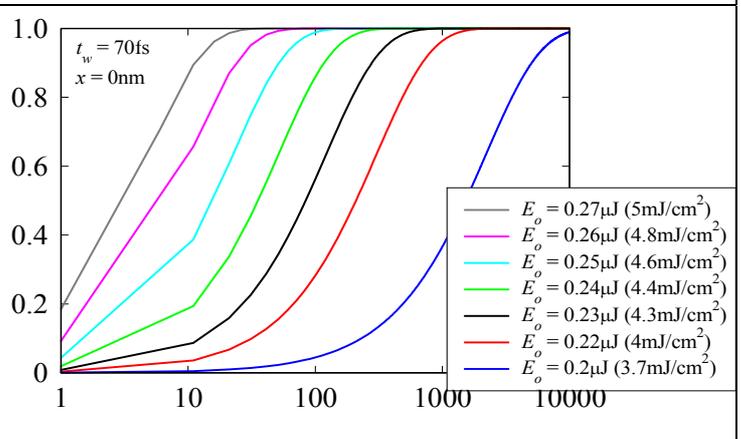

Fig. 10 Predicted fraction of crystallization of $Ge_2Sb_2Te_5$ optical disk sample subjected to multiple 70 fs pulses with energies in the range 0.2μJ to 0.27μJ.

5. CONCLUSION

Phase-change materials possess some remarkable properties and behaviour that can be used most effectively in a number of technological areas, from electrical and optical memories to, potentially, all phase-change arithmetic and cognitive processors. In this paper we have described theoretical and experimental investigations of some of these key application areas, with a view to providing insights into the possible future use of phase-change materials and the design of future phase-change devices and systems.

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