

Simulation Studies on Electrical, Thermal, and Phase-Change Behaviour of GeSbTe Based Memory Devices

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Abstract

Attempts at the practical utilization of Sb-Te based alloys beyond optical data storage have been made recently by employing these materials in both scanning probe type memories (similar to the IBM Millipede), and in electrical memory devices - namely Phase-Change Random Access Memory (PC-RAM). We have therefore developed models to simulate the electrical, thermal, and phase-change characteristics of this important class of material. In this paper we describe the physical basis of our models and present simulation results for different memory configurations and operating conditions.

1. Introduction

The application of phase-change alloys, for example GeSbTe and AgInSbTe, to optical data storage is now quite well established, with rewritable versions of the CD and DVD formats already on the market. Of course technology does not stand still, and development of even higher capacity phase-change based optical disks, such as the Blue-Ray system, is already underway. Phase-change materials also have many properties that make them suitable for electrical type memories; in particular the electrical resistivity varies by 3 or 4 orders of magnitude between the amorphous and crystalline states. This effect is being utilized in new solid state devices, the so-called PC-RAM (phase-change random access memory) chips that may offer a future alternative to conventional CMOS based memories. Yet another possibility is the use of phase-change materials in a scanning probe based storage system. The feasibility of a high density, high data-rate, scanned probe memory has already been demonstrated by IBM Zurich group via their Millipede system, where a 2-D array of around 1000 heated AFM-type tips write to and read from a polymer medium with bit sizes down to 50nm and less. The IBM polymer medium is essentially a write-once material, and it is natural to ask whether or not a similar concept of scanning probe based storage can be extended to known rewritable materials – in particular to phase-change media. Thus, it is clear that phase-change materials may find use in many different memory architectures, and it is therefore most desirable to have a thorough understanding of the electrical, thermal and kinetic processes that may be involved in such applications. For these reasons we are developing comprehensive and physically-realistic theoretical write-read models for this important class of materials.

2. Understanding the Phase-Change Process

2.1. Theory

A phase transformation starts with the formation of small regions of the new phase. As transformed regions continue to grow, however, they eventually impinge upon one another, slowing the rate of transformation. Typically this impingement is analysed following the approach suggested by Kolmogorov, Johnson and Mehl, and Avrami (JMAK analysis) [1,2]. This formalism has been in the past preferred to describe the phase-change processes of optical memories because of its simplicity. However, it is important to recognise that JMAK analysis is valid only for isothermal transformations. It should be used with caution for describing non-isothermal transformations. The most dramatic failures of the JMAK analysis appear when the assumption of random nucleation and growth is violated (as for example when ‘priming’ of the phase-change medium occurs). Also, for situations, where the material is heated or cooled rapidly on the time-scale required for atomic rearrangements, nucleation and growth of a new phase results in a time-dependent nucleation rate. In order to develop a physically-realistic phase-transition model to describe the time-dependent nucleation and growth we have used an approach

based on a full kinetic description of the phase-change process. Nucleation, growth and dissolution of the crystalline phase in an amorphous medium have been described using rate-equations. It is assumed that a crystalline cluster can grow or shrink by addition or loss of a single ‘molecule’ (or ‘monomer’). According to this scheme, one can write a differential equation for each cluster size to describe time-dependent density changes. Once all possible cluster sizes are considered then the complete description of the phase-change process is attainable.

We have assumed that the concentration $f(n,t)$ of clusters with (n) molecules can change by interactions of single molecules. One can easily envisage four possible reactions for a cluster of (n) molecules interacting with clusters of size $(n-1)$ and $(n+1)$ as illustrated in Fig. 1.

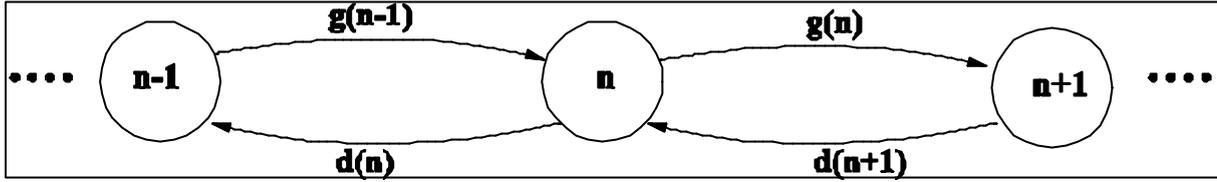


Figure 1. Possible growth and dissolution routes for a cluster of (n) monomers, depicted here schematically.

In view of these reactions we can write a kinetic rate-equation, that describes the development of the density of the clusters of size (n) :

$$\frac{\partial f(n,t)}{\partial t} = g(n-1,t)f(n-1,t) - d(n,t)f(n,t) - g(n,t)f(n,t) + d(n+1,t)f(n+1,t) \quad (1)$$

where $g(n,t)$ and $d(n,t)$ are reaction rate coefficients describing growth and dissolution of size (n) , respectively. Since one must consider all possible size of clusters, Eq(1) needs to be applied for $n=2$. For single molecules ($n=1$) the requirement of the conservation of matter in a given volume also requires that

$$f(1,t) = f(1,0) - \sum_{n=2}^{n_{\max}} n \cdot f(n,t) \quad (2)$$

where $f(1,t)$ is the concentration of monomers at a given time, and $f(1,0)$ is the initial monomer concentration. Here a summation over all possible cluster sizes, starting from smallest possible cluster size ($n=2$) to the largest (n_{\max}), is being carried out. It is possible for a large cluster to contain millions of molecules. For example, an easy calculation would show that a crystalline cluster of a few tens of nm of radius contains several millions of molecules of GeSbTe. This fact indicates that we need to consider several millions of coupled rate-equations for a successful simulation of crystallization.

To solve the set of rate equations it is necessary to know the growth and dissolution rates, $g(n)$ and $d(n)$, respectively. We modelled these rates by considering the atomic processes accompanying the phase-change. Following the theory of reaction rates [3] we assumed that the growth rate of a crystalline cluster of (n) molecules is governed by

- (i) The number of clustering monomers at an amorphous-crystalline interface; this is assumed to be proportional to the GeSbTe-monomer concentration determined by the density of material and the size of the cluster.
- (ii) The probability that a monomer overcomes the energy barrier at the amorphous-crystalline interface; this is written using Boltzmann statistics and is related to Gibbs free energy changes of phase-change process. The Gibbs free energy is assumed, to a first approximation, to be a sum of volume and surface energy terms.
- (iii) The trial-frequency of monomers to overcome the energy barrier; this is estimated from data on the viscosity of the material.

It is well known that the crystallization behaviour of a thin film of GeSbTe is strongly dependent on the substrate material on which GeSbTe is deposited [4]. This fact indicates that the nucleation of crystalline clusters takes place preferentially at the GeSbTe-substrate interface so that the phase-change process is not homogenous, where the nucleation may proceed randomly anywhere with equal probability, but heterogeneous, where energetically favourable places are preferential nucleation sites. In order to take into account the heterogeneous effects we modified the model by using the so-called ‘spherical-cap’ description [3]. Based on largely geometrical considerations, the spherical-cap model considers the nucleation to proceed at the substrate-GeSbTe interface by assuming the shape of nucleus to be a truncated sphere instead of a full sphere. The volume and the surface area of a nucleus are then determined not only by the radius but also by the angle between the nucleus surface and the substrate.

2.2. Results and Comparison to Experiment

We solved the model equations numerically by considering appropriate initial and boundary conditions. For all calculation results presented here the initial state of the GeSbTe was always amorphous, i.e., there were no crystalline clusters and only monomers were present. The number of rate equations n_{\max} was chosen sufficiently large so that the calculation results were not dependent on it. It was found that, depending on the thermal treatment, 10^4 to 10^7 rate equations were needed to simulate a given experiment. Unknown parameters of the model, the interface energy density between crystalline and amorphous phases and the angle describing the heterogeneous effects, were treated as fit parameters - values being found by experiment-simulation comparison. However, it should be noted that only a single set of fitting parameters were used for all the results presented (i.e. the fit parameters were identical for each and every simulation result).

For crystallization studies the change of optical properties (e.g. reflectance) of the material is often measured and this information is then related to the amount of material crystallized. Figure 2 shows such an experiment [5] where isothermal crystallization in a small range of temperature was measured. The material for these experiments was $\text{Ge}_2\text{Sb}_2\text{Te}_5$ deposited on a glass substrate. Simulations carried out to mimic these experiments could predict both total crystallisation times and the incubation times quite successfully. The model was capable of predicting the quite dramatic effect of rather small changes in annealing temperature on crystallization behaviour, as evidenced in Fig 2 where crystallisation times as well as incubation times change more than four-fold with a change of temperature less than 8°C.

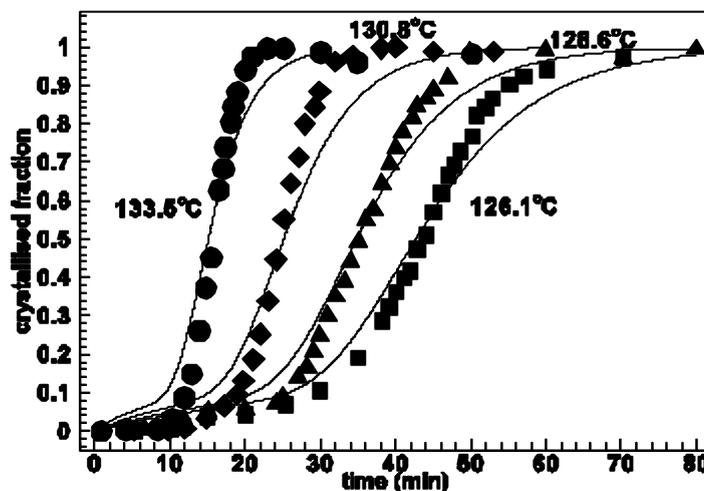


Figure 2 Experimental (symbols) [5] and simulated (lines) results of crystallization as a function of time for four different isothermal treatments.

Non-isothermal treatments, during which the temperature increases at a constant rate, are also common in the literature to study phase-change behaviour of GeSbTe thin films. Depending on the rate of temperature the onset of crystallisation shifts; the higher the rate, the higher the onset-temperature. Figure 3 shows published results from two different ramped-temperature experiments [6, 7] and our corresponding simulations results. In one case, where the ramp rate is 3°C/min, crystallisation takes off at about 155°C, while a ramp rate of 10°C/min results in a higher crystallisation-onset of about 180°C.

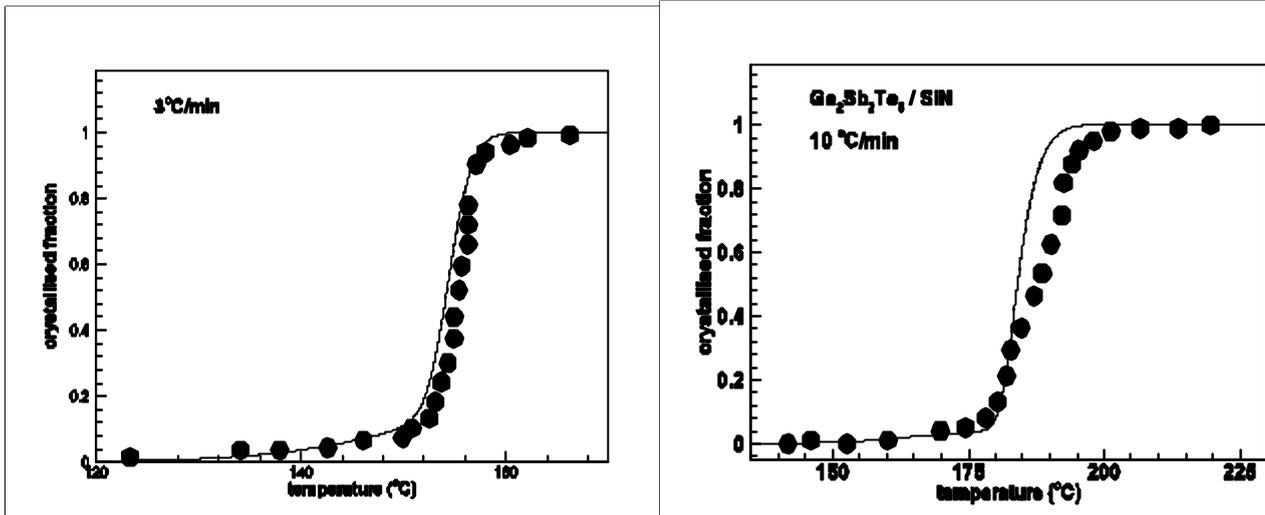


Figure 3 Experimental (symbols) and simulated (lines) results of crystallization during a ramped-temperature treatment. (Left) ramp-rate 3°C/min, substrate:silicon.[6]. (Right) ramp-rate 10°C/min, substrate:SiN [7].

As previously mentioned, the substrate on which the GeSbTe layer is deposited has a profound effect on crystallisation. Minute changes in surface conditions cause large effects in crystallisation kinetics. The onset of crystallisation and crystallisation times depend on substrate type and preparation. We could simulate such effects successfully as also seen in Fig 3. Since we could explain all heterogeneous effects with a simple ‘spherical cap’ model based on geometrical considerations, it is justifiable to argue that the main effect of a substrate on crystallisation kinetics is the change of energetics of the phase-change process. Instead of the formation of a nucleus in the shape of a whole sphere, for example, the GeSbTe-substrate interface offers preferential nucleation sites where a nucleus can form in the shape of a truncated sphere. Thus, the change of Gibbs free energy for nuclei formation, i.e., the driving force for crystallisation, is considerably increased.

3. Application to Scanning Probe Based Storage

The application of phase-change materials to optical data storage is now well known, with CD-R/W and DVD-R/W formats already on the market, and the so-called Blue-Ray, dual-layer, phase-change disk being developed by several companies. We, in collaboration with partners at CEA-LETI in Grenoble (France) and at Twente University (Netherlands), have also recently begun the development of a scanning probe type memory, similar in some respects to the IBM Millipede system, but using phase-change materials as the storage medium. The aim is to give a low-power, small form-factor memory with Terabit storage capability.

The basic mechanism of the phase-change based scanning probe storage system has a conductive AFM tip in contact with the storage medium. The writing process is an electro-thermal mechanism. When the current flows from the tip through the medium, the active layer is heated by the Joule effect. If the temperature increase is sufficient, the phase-change process takes place and the information is stored in the media as crystalline or amorphous dots. The readout process is performed by measuring the electrical resistivity of the structure. The amorphous and the crystalline states of the PC media are indeed characterised by very different electrical resistivities; in the case of the Ge₂Sb₂Te₅ alloy, the resistivity differs typically by four orders of magnitude. Figure 4 shows typical experimental results obtained so far (image courtesy of Yves Samson, Serge Gidon and Olivier Bichet, CEA-LETI Grenoble). However, the aim of this paper is to present theoretical studies of this novel form of scanning probe data storage; a thorough understanding of the physical phenomena involved in the write and read processes being crucial to the development and optimization of this new technique.

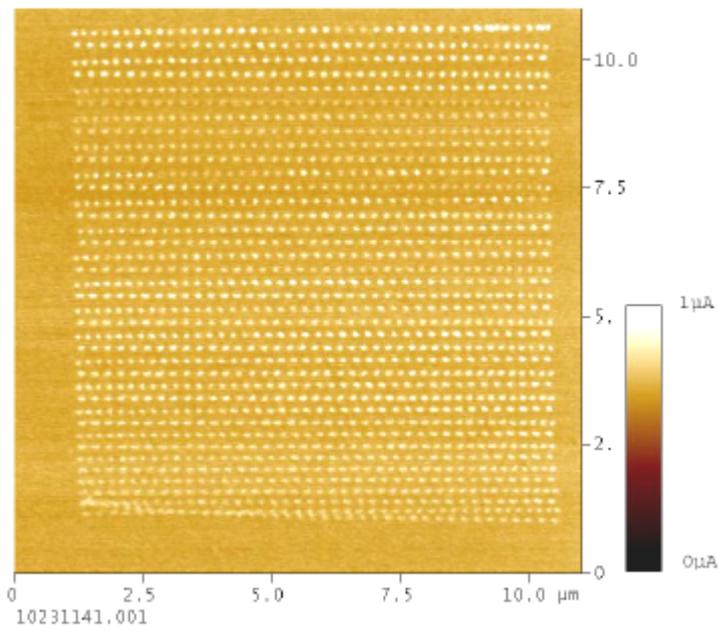


Fig.4 A 40 x 40 bit matrix obtained experimentally by applying 10 μ s, 7 V voltage pulses to a W₂C coated AFM tip scanned in contact with the medium. The bits are crystalline in an amorphous matrix. The image shows the electrical current difference between the amorphous and crystalline phases when scanning in contact with the same tip and applying a reading voltage of 4 V.

(the tilted bottom line corresponds to a false programming of the tip movement)

Image courtesy of Yves Samson, Serge Gidon and Olivier Bichet, CEA-LETI, Grenoble, France.

3.1. Theoretical model

The writing and the readout processes depend on the way the current flows in the structure. So one can expect important changes in the temperature distribution and consequently in the shape and size of the written dots, depending on the initial (amorphous or crystalline) state of the PC media. Thus, it is possible to write crystalline bits in an amorphous matrix, or amorphous bits in a crystalline matrix. We have considered both cases, to determine the best option with respect to the writing, the readout and the erasing processes.

In addition, the whole structure must be adapted for the electrical process as well as from a tribological point of view, since the tip is in contact with the sample. Besides, as in optical data storage, the GST layer must be protected from oxidation. For our purposes, a 30 nm thick GST layer is sandwiched between a capping layer and a (thermally and electrically) efficient under electrode. The three layers are deposited on top of a silicon substrate. We thus consider a 3-D geometry with cylindrical symmetry. A 2-D section is illustrated in Fig. 5.

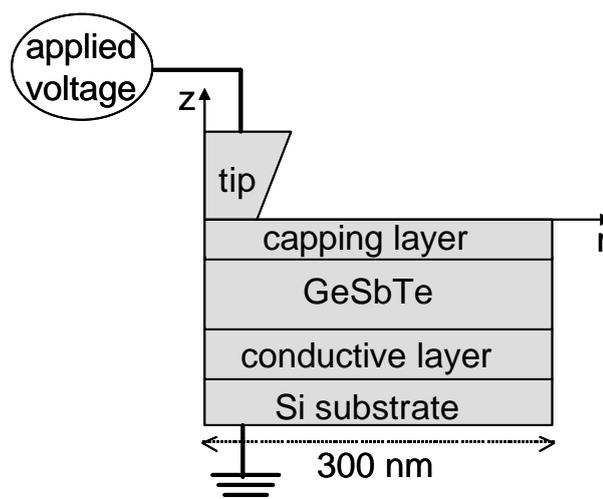


Fig. 5 2-D section of the geometry used in the simulation program

The electro-thermal process is modelled by solving the Laplace and heat-diffusion equations for the system, i.e.:

$$\nabla \cdot (\mathbf{s} \cdot \nabla V) = 0 \quad (3)$$

$$\rho C_p \frac{\partial T}{\partial t} - K \cdot \nabla^2 T = \mathbf{s} \cdot \mathbf{E}^2, \quad (4)$$

where σ is the electrical conductivity, V the electrical potential and E the electric field; ρ , k , and C_p correspond respectively to the density, the thermal conductivity and the specific heat. The calculations were performed using a finite element method to analyse the current flow and the temperature distribution in the structure, when a voltage was applied at the top of the tip and the bottom of the structure was maintained at ground potential.

3.2. Simulation Results

Before modelling the whole writing process, it was important to evaluate the influence of the thickness and the properties of the different layers. In particular, we should determine the characteristics of the capping layer that enable enough current to flow in the GST layer, such that the temperature increase is sufficient to initiate the phase-change process. As mentioned above, both the amorphous and the crystalline phases are considered as potential initial state of the GST material.

At room temperature, the electrical conductivity of the amorphous state is only about $0.1 \Omega^{-1}m^{-1}$, but increases with temperature and electric field. For the crystallisation process, a temperature of around $200^\circ C$ is required. The crystalline state is characterised by a high conductivity ($\approx 1000 \Omega^{-1}m^{-1}$ at room temperature), which is also temperature dependent. In this case, a temperature of about $650^\circ C$ is needed to amorphize the material. We performed a parametric study to evaluate the maximum temperature in the GST layer (when the system reaches its steady state) as a function of the electrical conductivity of the capping and the GST layer. The thickness of the capping layer was set to 1.5 nm and the applied voltage $10V$. The results are presented in Fig. 6. It can be seen that the maximum temperature is highly dependent on the electrical conductivity of the capping layer, since it ranges from $50^\circ C$ to $1600^\circ C$. The temperature increases with the conductivity of the GST layer, as the current flows preferentially towards the most conductive regions. A capping layer conductivity of $50 \Omega^{-1}m^{-1}$ is suitable for achieving the required temperature in the GST layer for the writing of both crystalline and amorphous bits.

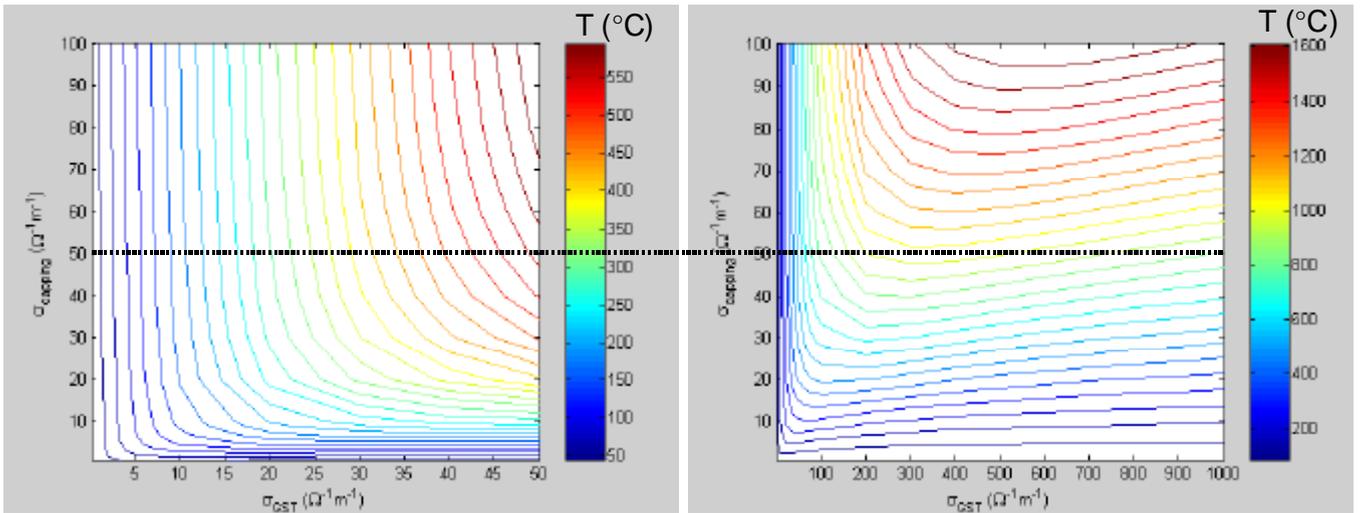


Fig. 6: Maximum temperature in the GST layer as a function of the electrical conductivity of the capping and the GST layers; left – writing crystalline bits in amorphous matrix; right – writing amorphous bits in crystalline matrix

In the results presented above, the value of electrical conductivity of the GST layer was kept constant. In reality, the GST conductivity depends on both temperature and electric field values at any instant in time, and this should be taken into account for realistic modelling. These dependencies for the amorphous and the crystalline phases are expressed respectively by:

$$\mathbf{s}(T, E) = \mathbf{s}_{0_am} \times \exp\left(-\frac{\Delta \mathbf{x}_{am}}{kT}\right) \times \exp\left(\frac{E}{E_0}\right) \quad (5)$$

$$\mathbf{s}(T) = \mathbf{s}_{0_cryst} \times \exp\left(-\frac{\Delta \mathbf{x}_{cryst}}{kT}\right), \quad (6)$$

where $\Delta \xi$ is the activation energy ($\Delta \xi_{am} = 0.3\text{eV}$, $\Delta \xi_{cryst} = 0.04\text{eV}$), and σ_{0_am} and σ_{0_cryst} are taken to be $1.9 \times 10^4 \Omega^{-1}\text{m}^{-1}$ and $5 \times 10^3 \Omega^{-1}\text{m}^{-1}$ respectively. These parameters were determined by fitting to experimental data. E_0 is a constant field normalisation factor.

Such expressions were introduced in the simulation program, to compare the temperature distribution in the GST layer. The temperature distribution at the end of a 100 ns writing pulse is illustrated in Fig. 7. Depending on the initial state of the GST material, a great difference in the maximum temperature is observed. 160°C and 1600°C are reached respectively from the amorphous and the crystalline starting phase. This is due to the difference in the value of the corresponding conductivities. But the graphics point out also that the temperature is not distributed in the same way. Starting with an amorphous material (see Fig. 7a), the hottest area is located in the middle of the GST layer and the temperature distribution spreads through the thickness. On the contrary, when the GST material is initially crystalline (see Fig. 7b), the maximum temperature is reached at the top of the layer, just below the tip.

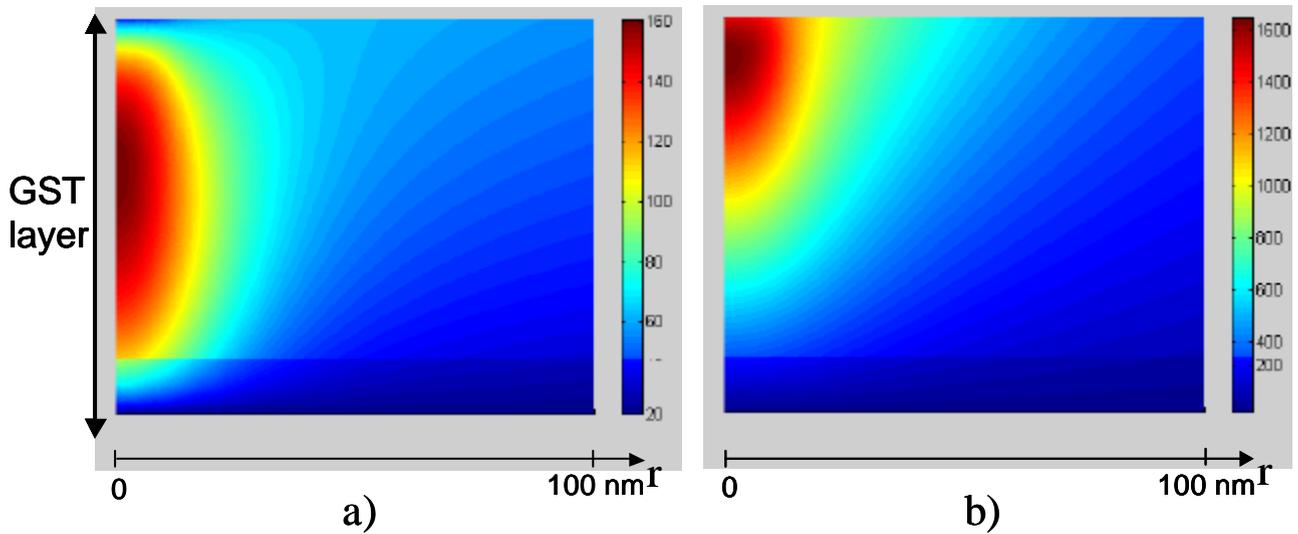


Fig. 7 Temperature distribution in the GST layer at the end of the writing pulse a) from the amorphous state ($E_0 = 3 \times 10^9 \text{V/m}$), b) from the crystalline state

The analysis of the temperature distribution gives information on the expected shape and size of the written dots. The results presented here suggest that the crystalline dots will spread through the thickness of the GST layer, whereas the amorphous dots will be more localised at the top of the layer. Important effects on the readout contrast, and, importantly, on the feasibility of the erasing process can then be expected for such a probe-storage system, depending on the choice of the initial state of the GST material. Such considerations are now being investigated.

The next stage of this work is to combine the electro-thermal model with the phase-transition model (or at least a simplified but physically realistic version of the phase-change model) into a full write/read model. This work is ongoing.

4. Conclusions

We have developed a comprehensive model for the electrical, thermal and phase-change processes involved in novel storage applications of phase-change alloys, in particular for GeSbTe. The phase-transition model itself is based on the classical nucleation theory and accounts for the kinetics of phase-change by using rate-equations. In the model formation of crystalline clusters has been described by a set of rate equation. Rate coefficients of these equations have then been modelled by considering the molecular processes taking place during phase-change process. This model has been then used in a calculation programme to simulate crystallisation behaviour of GeSbTe. In particular we simulated successfully experiments involving isothermal and non-isothermal treatments. It has been shown that the model is capable of explaining the effects of minute temperature changes, influences of different substrates on which GeSbTe was deposited, and the role of transient nucleation and growth.

The application of phase-change materials to novel forms of storage architecture has been investigated, in particular to scanning probe type memory. A model for the write and read processes in such an application has been developed, which, when combined with the phase-transition model, can give a full and physically realistic description of the complex electrical, thermal and kinetic behaviour of this interesting class of materials.

Acknowledgements

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