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Stress Limited Scaling in $Ge_2Sb_2Te_5$

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ABSTRACT

The influence of stress on the phase change behaviour of $Ge_2Sb_2Te_5$ encapsulated by ZnS-SiO_2 and TiN is investigated using temperature dependent Extended X-ray Asbsorption Fines Structure and Ellipsometry to determine the crystallisation temperature. The encapsulation material surrounding the $Ge_2Sb_2Te_5$ has an increasingly dominant effect on the material's ability to change phase and can cause a profound increase in its crystallization temperature. We have experimentally shown that the increased crystallization temperature originates from compressive stress exerted from the encapsulation material. By minimizing the stress we have maintained the bulk crystallization temperature in $Ge_2Sb_2Te_5$ films just 2 nm thick.

INTRODUCTION

Phase Change RAM (PCRAM) is a memory technology which, unlike the current silicon based technologies, does not suffer from problems associated with the storage of charge. Data is stored in the form of structural differences in a thin film of the material. $Ge_2Sb_2Te_5$ is the leading candidate material for such technology[1] and changes in its rate of crystallization have been observed for films thinner than 30 nm however the true limit to which $Ge_2Sb_2Te_5$ can be scaled yet still retain the ability to crystallise needs to be proven. Scaling $Ge_2Sb_2Te_5$ to smaller volumes has the added virtue that the switching power, accomplished by Joule heating, linearly improves with reducing cell size [2]; clearly this is beneficial with respect to the recent increase in portable devices which require large solid state memories.

$Ge_2Sb_2Te_5$ can exist in two crystalline phases, the metastable cubic phase, and the equilibrium hexagonal phase; in addition it can also exist in an amorphous phase. The cubic and hexagonal phases are formed by increasing the temperature of the as-deposited amorphous material to approximately 150 °C and 300 °C respectively. Substantial optical and electrical differences manifest as a result of the atomic scale structural differences between the amorphous and cubic crystalline phases; generally, the crystalline phase exhibits a higher refractive index, optical absorption and electrical conductivity in comparison to the amorphous phase. Clearly, changing phase between the amorphous and the metastable cubic crystalline state causes a large optical and electrical contrast which can be utilized for data storage applications[3].

Raoux et al. studied *in situ* x-ray diffraction from ultra-thin films of $Ge_2Sb_2Te_5$, GeSb and SbTe as a function of temperature[4, 5]. It was found that for $Ge_2Sb_2Te_5$ films capped

with Al_2O_3, the crystallization temperature sharply increased with decreasing film thickness. But since long range order is necessary to achieve diffraction this technique is challenging for thin films. In contrast Extended X-ray Absorption Fine Structure (EXAFS) probes the local structure around a specific chemical species within a material. Typically only the first or second nearest neighboring atoms contribute to the EXAFS signal hence the technique is sensitive to very thin films of material. Background subtracted EXAFS spectra as a function of momentum transfer are denoted as χ(k). The EXAFS spectra for the Ge K-edge in $Ge_2Sb_2Te_5$ shows significant, characteristic, differences between the crystalline and amorphous states which have been attributed to an octahedral to tetrahedral coordination change in the Ge atoms position [6] and a corresponding change from resonant to covalent bonding[7]. These differences are most apparent at the momentum value k=3.3 $Å^{-1}$ (see reference [8]) and can therefore be used as fingerprints to monitor changes in local bonding arising during crystallisation. For this reason, *in-situ*, temperature dependent, EXAFS is an ideal technique to determine the phase transition temperature of $Ge_2Sb_2Te_5$ thin films[8].

EXPERIMENTAL DETAILS

$Ge_2Sb_2Te_5$ films were sandwiched with two different materials; $(ZnS)_{0.85}(SiO_2)_{0.15}$, commonly used in phase change optical discs, and TiN which is used as the electrode material in PCRAM cells. The stress induced by both cladding materials was analyzed using a high resolution x-ray diffractometer to measure the change in incident angle necessary to diffract from the (0 0 4) plane of a silicon substrate of thickness 650μm. This technique is described elsewhere[9]. The induced stress was analyzed using Stoney's equation [10] via the substrate curvature; a Young's modulus, E, of 126 GPa and σ=0.3 was used for the Poisson ratio[11] of the substrate. The films were 100 nm thick; as confirmed by X-Ray Reflectivity (XRR). Since the films were significantly less than 1% of the substrate thickness it was not necessary to employ any correction factors[10]. The calculated stress on the $Ge_2Sb_2Te_5$ layer from 20 nm thick films of $(ZnS)_{0.85}(SiO_2)_{0.15}$ and TiN was found to be 58 MPa and 240 MPa respectively. $Ge_2Sb_2Te_5$ films of thicknesses varying between 2 nm and 10 nm were sputtered at 0.5 Pa and 30 W thus creating a $(ZnS)_{0.85}(SiO_2)_{0.15}$ or TiN cladded structure atop of a quartz substrate. The thickness, density and surface roughness of the resultant structure was obtained by measuring XRR and fitting a model to the experimental data using the Motofit code[12]. The procedure allowed for sub-nanometer accurate measurements of all layers and the ability to check for the presence of interfacial phases. The XRR analysis confirmed that the density of the thin films and the interface roughness as a fraction of thickness remained constant implying that the films are continuous even at the thinnest extreme.

EXAFS spectra were collected between 130°C and 200°C at intervals of 5°C. During the measurement the sample temperature was held constant and controlled to within 1°C. Soller slits and Al filters were put between the sample and a muliple element solid state detector allowed a decrease in background fluorescence. The resultant scans were Fourier filtered using the Athena [13] program before subtracting the 130°C scan (baseline) to show subsequent changes in the spectra. A change in atomic structure is evident as a large change in χ at a particular temperature, for thicker films this change took place at approximately 170°C, see Fig. 1.

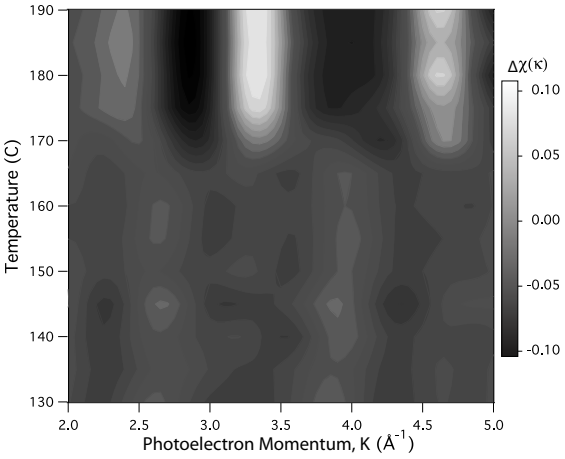

Figure 1. EXAFS spectra plotted as a function of temperature for 6 nm of $Ge_2Sb_2Te_5$ sandwiched between 20 nm of ZnS-SiO_2 film.

In addition to these structural measurements, temperature dependent ellipsometry at 633 nm was also carried out on the films for the fixed angle of 70°. At the phase transition, the ellipsometric parameters, Δ and Ψ, which are related to the change in phase between the P- and S- polarization states upon reflection, show a discontinuity which arrises due to a convoluted effect of changes in the materials dielectric properties and thickness[8].

Both the EXAFS and Ellipsometry results show that the crystallization temperature of $Ge_2Sb_2Te_5$, enclosed by TiN, rapidly increases from 165°C to 299°C for films of thickness decreasing from 6 nm to 2 nm. A similar trend was observed by Raoux et al. for $Ge_2Sb_2Te_5$ capped by Al_2O_3[4]. The results of both temperature dependent EXAFS and ellipsometry have been plotted on the same axes in Fig. 2. It can be seen that the crystallization temperature rise is not a universal observation for all cladding materials. Enclosing the $Ge_2Sb_2Te_5$ layer with $(ZnS)_{0.85}(SiO_2)_{0.15}$ allowed the material to crystallize at temperatures close to those measured for thicker films and, in contrast, a small decrease in the crystallization temperature could be achieved by reducing the $Ge_2Sb_2Te_5$ thickness from 6 nm to 2 nm. A second discontinuity was also observed in the ellipsometric parameters at temperatures decreasing from 259 °C to 229°C as the film thickness was reduced to 2 nm; corresponding to temperature range of the cubic - hexagonal phase transition[8].

DISCUSSION

TiN has been shown to increase the crystallization temperature whereas, $(ZnS)_{0.85}(SiO_2)_{0.15}$ allows the $Ge_2Sb_2Te_5$ to crystallize at slightly lower temperatures with decreasing film thickness. The glass transition temperature, T_g, is the minimum temperature at which atoms within an amorphous matrix can rearrange to form a lower free energy structure. At the glass transition temperature the stresses within the $Ge_2Sb_2Te_5$ film are reduced by viscous flow and this has been observed above 100°C for uncapped $Ge_2Sb_2Te_5$ [14]. If a tensile stress

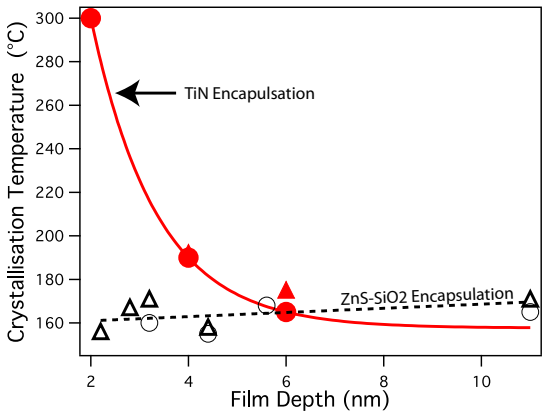

Figure 2. Crystallization temperature as a function of film thickness. The results for the TiN encapsulation are indicated by filled shapes and unfilled shapes indicate $(ZnS)_{0.85}(SiO_2)_{0.15}$ encapsulation. Measurements obtained by EXAFS are given by circles and measurements obtained by ellipsometry are plotted as triangles.

is applied to $Ge_2Sb_2Te_5$, the pressure within the $Ge_2Sb_2Te_5$ film will be reduced and conversely increased in the case of compression. As mentioned earlier, the stress induced from the cladding layers of the $Ge_2Sb_2Te_5$ films in this experiment was found, in the case of 20 nm of TiN, to be 240 MPa. In such a case, the compression originating from the cladding restricts the crystallization kinetics by increasing the activation barrier between the two phases, perhaps by diminishing the process of covalent bond rupturing during the passage of the Ge atom from tetrahedral to octahedral Te coordination. Higher temperatures are therefore necessary for the material to crystallize. Published data also supports the idea that the crystallization activation energy can increase with decreasing film thickness[15]. We believe the stress from the encapsulating material is responsible for the observed increase in activation energy.

By using a $(ZnS)_{0.85}(SiO_2)_{0.15}$ encapsulating material which applies a lower compression of 58 MPa, a slight decrease in crystallisation temperature with decreasing films thickness was measured for both the cubic and hexagonal transitions. Assuming the aforementioned idea of compression dependent crystallisation activation energy, one would expect a small rise in the crystallisation temperature. This suggests that the as-deposited $Ge_2Sb_2Te_5$ film has some intrinsic tensile stress. Even with the 58 MPa applied from the encapsulating $(ZnS)_{0.85}(SiO_2)_{0.15}$, the intrinsic tensile stress is sufficient to cause a reduction in the crystallisation temperature. To explain this behaviour, the magnitude of intrinsic stress within the film must also be thickness dependent.

Proper analysis of the phase change thermodynamic cycle[8] with respect to the applied stress allows one to formulate principles of design for increasingly small memory scales. For example, if sub 10 nm $Ge_2Sb_2Te_5$ memory cells are to be implemented to replace non-volatile, charge storage, Flash-type memories, the issue of cyclability is arguably of less importance than that of electrical efficiency and therefore a cladding material which minimizes the

crystallization temperature by reducing the compressive stresses on the $Ge_2Sb_2Te_5$ would be more appropriate. However, if electrical efficiency is of lower importance and cyclability is the prime goal of the memory cell, a highly compressive cladding material, like TiN would be more suitable. This would be the case for DRAM replacement where essentially an infinite number of cycles are required. A highly compressive cladding material has the added advantage that the energy required to crystallize the material increases with decreasing cell dimensions and therefore aids the problems associated with thermal cross-talk and archival stability of the materials, this is opposite to conventional DRAM.

CONCLUSION

The cladding layers encapsulating the $Ge_2Sb_2Te_5$ play an increasingly important role as the cell dimensions are reduced beyond 10 nm and films just 2 nm thick are able to crystallise at temperatures close to that of their bulk crystallisation temperature. We have found that compressive stress increases the energy required for the transition atomic rearrangements thus increasing the crystallization temperature. Materials such as TiN and Al_2O_3 tend to cause a sharp increase in the crystallization temperature whereas $(ZnS)_{0.85}(SiO_2)_{0.15}$ which applies a lower stress has a negligible effect on the crystallization temperature. These insights have allowed us to identify essential design criteria to enable $Ge_2Sb_2Te_5$ memory cells to be scaled to their physical, phase change limit.

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