

Enhanced crystallization of GeTe from an Sb₂Te₃ template

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Crystalline Sb₂Te₃ templates reduce the crystallization time of the phase change material GeTe by four orders of magnitude to 20 ns. Structural measurements and density functional theory molecular dynamics atomistic modeling show that this reduction is a direct consequence of textured crystal growth from a plane of octahedral crystal nucleation centers. The nucleation template serves to reduce the crystallization activation energy by 2.6 eV allowing crystallization to proceed at a temperature 95 °C lower than that of the untemplated GeTe film. © 2012 American Institute of Physics. [doi:10.1063/1.3675635]

Phase change materials can store data as amorphous or crystalline atomic arrangements where the short range structural differences give rise to substantial contrast in the electrical and optical properties.¹ In order to switch from the amorphous to the crystalline states, the constituent atoms must gain sufficient energy to form a thermodynamically stable crystalline nucleus within an amorphous matrix. For electrical phase change random access memory (PCRAM) applications, this energy is usually supplied by Joule heating.² Traditionally, phase change materials have been improved by trial and error of different compositions and dopants. In contrast, herein, a crystallization nucleation template is shown to reduce the crystallization time of GeTe by four orders of magnitude and substantially lower the energy necessary to crystallize the material.

Interfacial effects are known to influence the crystallization of phase change materials.^{3,4} In real PCRAM devices, interfacial effects dominate as the encoded volume of material is reduced in order to meet the demands of high density data storage.⁵ It is, therefore, necessary to understand and control the affect of interfaces on the phase change properties. Recently, molecular dynamics simulations demonstrated heterogeneous crystal growth from an interfacing lattice matched template.⁶ Until now, however, this concept has not been experimentally verified. The crystallization time of phase change compounds that exist along the technologically relevant Sb₂Te₃-GeTe tie-line (including Ge₂Sb₂Te₅) is dominated by the rate that crystal nuclei are formed in the amorphous material;⁷ the rate of crystal growth is relatively low. These materials are, therefore, called nucleation dominated phase change materials. Heterogeneous templated crystallization provides a mechanism to reduce this time consuming nucleation process thus increasing the rate that data can be transferred to the material.⁸ In this paper, a crystalline (*crys*-) Sb₂Te₃ template layer is shown to reduce the crystallization time of GeTe by four orders of magnitude. Structural measurements and molecular dynamics models demonstrate that these substantial enhancements are a corollary of templated crystallization.

High temperature (250 °C) helicon-wave sputter deposition was used to grow 5 nm thick rhombohedral *crys*-Sb₂Te₃, with a high degree of orientation along the [001] crystallographic axis, on top of fused silica substrates. The *crys*-Sb₂Te₃ was then allowed to cool naturally for 16 h under a vacuum of $<1 \times 10^{-4}$ Pa. An amorphous GeTe layer was then deposited on top of the *crys*-Sb₂Te₃.

Here, it is hypothesized that the rhombohedral, R $\bar{3}m$ (hexagonal setting) of *crys*-Sb₂Te₃ presents a [001] plane of unoccupied octahedrally coordinated sites. Depositing *am*-GeTe atop of textured *crys*-Sb₂Te₃ provides, therefore, a means to artificially fabricate octahedral nucleates (4-fold rings) at the interface of the two layers. Considering simplified models^{9,10} of the switching process in phase change materials, the crystallization of *am*-GeTe deposited atop of [0 0 1] Sb₂Te₃ would involve the Ge atoms relocating from a mixture of lower coordination sites to octahedral positions at the Sb₂Te₃ interface.¹¹ These Ge atoms would then act as stabilized crystal nucleation centers thus avoiding GeTe's time consuming nucleation process. A corollary of this hypothesis is that the crystallographically textured *crys*-Sb₂Te₃ layer would then act as a template for subsequent growth of a textured GeTe crystalline film.

The crystallization temperature of amorphous GeTe films, which were deposited directly atop of the 5 nm *crys*-Sb₂Te₃ film and the silica substrate, was measured by monitoring the transmitted intensity of visible light through the films as a function of temperature, see Fig. 1(a). The abrupt decrease in transmission corresponds to the crystallization of the film. The *am*-GeTe films that were grown on the fused quartz substrate crystallized at 240 °C. In contrast, the crystallization temperature was reduced to 145 °C (a significant 95 °C reduction) for the *am*-GeTe that was grown on top of the *crys*-Sb₂Te₃ layer. Kissinger analysis of the crystallization activation energy was performed for temperature ramps of 2, 5, 7.5, and 10 K min⁻¹, see Figure 1. A total (nucleation and growth) crystallization activation energy of 4.4 eV was measured for the samples grown on fused quartz however, this energy was substantially reduced to 1.8 eV for GeTe grown on the *crys*-Sb₂Te₃ layer. By comparing these values with the reported 1.77 eV growth activation energy of a GeTe crystal,¹² it appears that the activation energy for the

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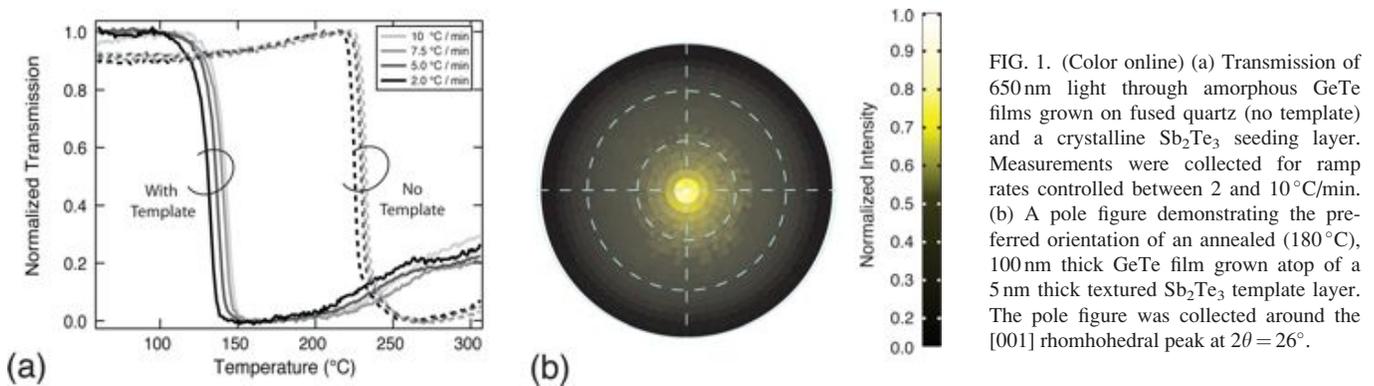


FIG. 1. (Color online) (a) Transmission of 650 nm light through amorphous GeTe films grown on fused quartz (no template) and a crystalline Sb_2Te_3 seeding layer. Measurements were collected for ramp rates controlled between 2 and 10 °C/min. (b) A pole figure demonstrating the preferred orientation of an annealed (180 °C), 100 nm thick GeTe film grown atop of a 5 nm thick textured Sb_2Te_3 template layer. The pole figure was collected around the [001] rhombohedral peak at $2\theta = 26^\circ$.

crystal nucleation alone in the Sb_2Te_3 -GeTe structure is negligible; the measured 1.8 eV is the activation energy required for growth alone. This is reasonable since, octahedral crystalline seeds were artificially formed at the GeTe- Sb_2Te_3 interface. The crystallized Sb_2Te_3 -GeTe film had a strong preferred orientation along the [001] direction, which corresponds to a pseudo-cubic [111] direction, see the x-ray pole figure displayed in Figure 1(b). This indicates that the crystallization process takes place from the interface thus causing non-random, fiber-like texture in the x-ray diffraction (XRD) pattern; an additional benefit of templated crystallization. Rietveld analysis of the templated GeTe XRD spectra revealed a $R\bar{3}m$ structure with the cell parameters $a = 4.144 \text{ \AA}$ and $c = 10.618 \text{ \AA}$. Since both the a and c crystallographic axes are compressed relative to the measurements made on the unseeded GeTe film ($a = 4.162 \text{ \AA}$ and $c = 10.666 \text{ \AA}$) and considering the formation energies of vacancies in GeTe,¹³ it is likely that the seeded structure contains a higher proportion of vacancies than that reported for unseeded GeTe.¹⁴

The aforementioned lowering of activation energy was attributed to a nucleation free crystallization process since the plane of $\text{crys-Sb}_2\text{Te}_3$ provides a stable heterogeneous interface from which crystal growth can occur. One would, therefore, expect the crystallisation process in these templated GeTe materials to be transferred from a process dominated by the nucleation rate to a process dominated by the crystal growth rate. Thus, a decrease in the overall crystallization time of Sb_2Te_3 templated GeTe is to be expected. To check this, a pump-probe laser static tester^{11,15} was used to measure the minimum crystallization time of $\text{crys-Sb}_2\text{Te}_3$ templated GeTe and untemplated GeTe. Figure 2 shows the transmission of the probe laser beam as a function of time and pump power through an amorphous 20 nm thick GeTe film deposited on a 5 nm thick Sb_2Te_3 template layer. The pump laser pulse was initiated at 0 ns and its duration was 200 ns. The darkest area indicates a decrease in transmission and is attributed to crystallization. Assuming complete crystallization corresponds to a saturated change in the film transmission, it can be seen that complete crystallization can occur in just 20 ns for an incident optical power of 20 mW. A similar measurement was repeated for a 20 nm thick GeTe film deposited directly on top of the fused quartz substrate but crystallization was not possible within the 1000 ns probe duration of the static tester apparatus. Measurements per-

formed by Raoux *et al.*¹⁶ on films of a similar thickness have shown that as-deposited GeTe crystallizes in 100 μs .

These measurements show that the Sb_2Te_3 template layer reduces the total crystallization time of as-deposited GeTe by a factor of 10^4 . Naturally occurring nucleation centers that form as a result of laser amorphization of the crystalline phase can also reduce the crystallization time from 100 μs to 200 ns.¹⁶ Herein, the samples were artificially engineered such that a plane of octahedral nucleation centers interface with the GeTe thus reducing the crystallization time yet further to 20 ns. The crystallization time was measured to be independent of the GeTe film thickness, for thicknesses between 10 nm and 50 nm (thickness range imposed by the 650 nm laser radiation absorption length), thus the crystal growth rate must be greater than 2.5 ms^{-1} . This independence of film thickness might, at first glance, suggest a nucleation dominated crystallization process, however, the authors believe the crystallization process is similar to that reported in GeTe PCRAM cells⁵ where growth precedes from the crystalline surroundings and the growth rate dominates. Indeed, complete recrystallization of amorphized volumes embedded in a crystalline film were possible in 16 ns,⁵ in good agreement with the templated crystallization times described herein.

Density functional theory molecular dynamics (DFT-MD) models, using a generalized gradient approximation

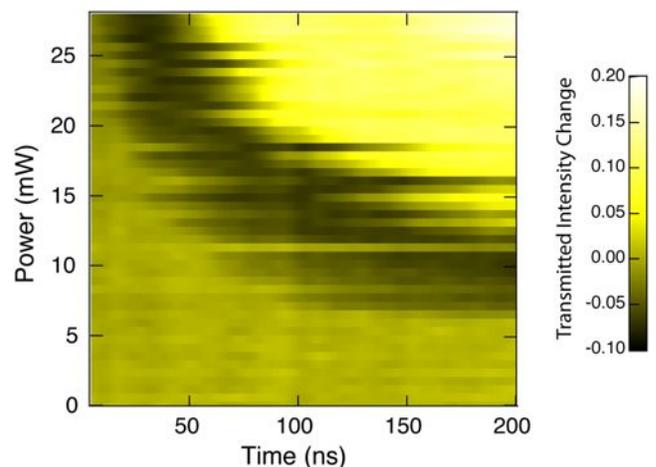


FIG. 2. (Color online) Probe laser beam transmission through GeTe interfaced with Sb_2Te_3 for different pump laser beam powers.

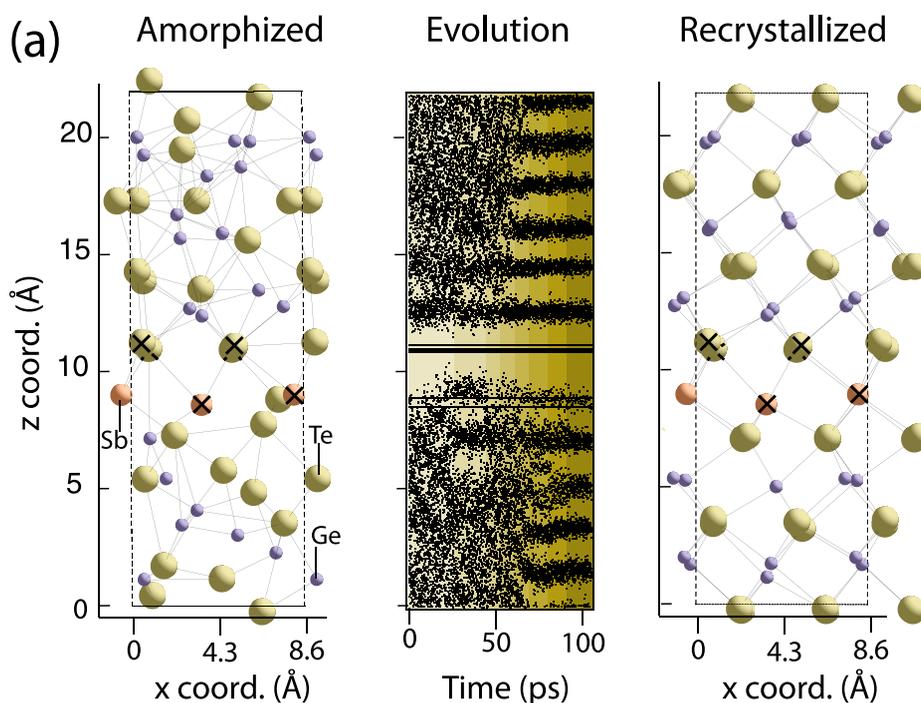
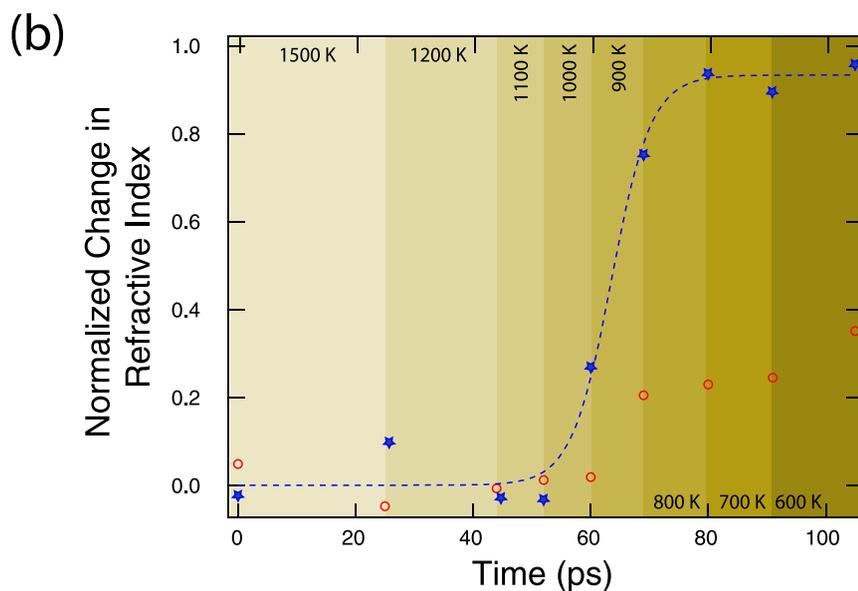


FIG. 3. (Color online) Analysis of molecular dynamics models of GeTe and GeTe interfaced with Sb_2Te_3 . The upper scatter plot shows the z coordinate of the atoms within the templated GeTe sample (a). The Sb_2Te_3 template atoms are fixed and are marked with a \times . Periodic boundary conditions are present at $z=0\text{ \AA}$ and $z=21.9\text{ \AA}$ and $x=0\text{ \AA}$ and $x=8.6\text{ \AA}$. The lower plot shows the change in refractive index normalized against the perfect crystals refractive index at 650 nm as a function of the model's time for Sb_2Te_3 -templated GeTe (stars) and pure GeTe (circles) models (b).



within the density functional code CASTEP,¹⁷ have allowed the relative effect of Sb_2Te_3 on the crystallization of GeTe to be compared with a pure GeTe model. The templated model was formed from a 48 atom GeTe structure, replacing a plane of 4 Ge atoms with 2 Sb atoms and 2 vacancies, then relaxing the structure at 0 GPa and 600 K for 2 ps. The Sb_2Te_3 -templated and pure GeTe cells had approximately the same cell width and were, therefore, subject to the same periodic boundary conditions, thus comparisons are valid. The structure was amorphised with the Sb_2Te_3 template's atomic positions fixed and melting the remaining structure within a constant volume at 2000 K. This is twice the melting temperature of GeTe thus the influence of the non-melting template layer was considered negligible. The system was

allowed to exponentially cool from 2000 K to 600 K over period of 105 ps. A scatter plot of the atomic positions projected onto the unit cell z -axis during the cooling is given in Figure 3(a). Although atomic movements are three dimensional, the crystal growth occurs in one dimension and the whole cell is crystallized in the period between 50 ps and 75 ps. Thus, the 1-dimensional crystal growth rate is estimated to be 80 ms^{-1} ; a reasonable value if one considers experimental growth rate estimates for other phase change materials.¹⁸ The modeled crystal grows from the plane of locked Te atoms and Sb atoms serve to stabilize the seeding layer. The modeled refractive index for pure GeTe and Sb_2Te_3 -templated GeTe was then calculated at various points during the model's evolution by applying a dipole approximation.

Figure 3(b) shows the change in refractive index normalized against the value calculated for the perfect crystal. For the templated model, crystal growth brings about a substantial increase in structural order thus permitting resonant bonding and a corresponding increase in the modeled refractive index.^{1,10,15,19} Comparing the normalized change in refractive index of both the templated and untemplated models after 105 ps, the recrystallized templated model's refractive index reaches almost the same level as that of the perfect structure. In contrast, after 105 ps, the pure GeTe model shows just 30% of the change necessary to reach that of the perfectly crystalline model. Optically, the pure GeTe model cannot be considered fully crystalline.

In the system modeled here, the amorphous state was formed by melting the crystalline material. In a real device, however, this may lead to long range atomic diffusion and loss of the template layer. Employing interfacial phase change materials (iPCM),¹¹ however, results in a material that allows a non-melting phase transition. All of the GeTe/Sb₂Te₃ iPCM structures reported in Ref. 11 were grown atop of 5 nm thick *crys*-Sb₂Te₃ template layers with strong preferred orientation along the pseudo-cubic [001] hence establishing preferred orientation in the iPCM structure. Devices based on these materials were faster, more cyclable and had a substantially lower programming energy than their unstructured Ge₂Sb₂Te₅ counterpart.

The experimental results, reported here, add experimental weight to the calculations of Akola and Jones and Hegedus and Elliott whom showed the crystallization of Ge₂Sb₂Te₅ involves the initial formation of 4-fold rings which serve as octahedral nucleation seeds for cubic crystal growth.^{20,21} Our atomistic modeling and structural measurements have confirmed that this reduction in crystallization time in GeTe-Sb₂Te₃ pseudo-binary systems can be directly attributed to the nucleation centers provided by the nanoscale *crys*-Sb₂Te₃ template. The crystal nucleation time of GeTe was reduced and complete crystallization of films up to 50 nm thick occurred in just 20 ns. The templated crystallization technique serves as a practical means to control the phase change process and limit crystal growth to a single axis. This inherent control has enabled the development of

high performance nano-engineered materials where templated growth of GeTe limits the crystal growth direction to a single dimension.

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