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Schottky barrier formation at amorphous-crystalline interfaces of GeSb phase change materials

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The electrical properties of amorphous-crystalline interfaces in phase change materials, which are important for rewritable optical data storage and for random access memory devices, have been investigated by surface scanning potential microscopy. Analysis of GeSb systems indicates that the surface potential of the crystalline phase is ~ 30 – 60 mV higher than that of the amorphous phase. This potential asymmetry is explained qualitatively by the presence of a Schottky barrier at the amorphous-crystalline interface and supported also by quantitative Schottky model calculations.

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Rewritable optical disk technology, well known from the CD, DVD, and Blu-ray disk formats, has been matured during the last two decades and has shown considerable progress. For example in 2007 alone, ~ 10 billion rewritable optical disks were sold, which were used to read, write, and erase data.¹ These erasable optical disks employ phase change materials (PCMs)¹ to store data by reversibly transforming local material volumes between the amorphous and the crystalline state. A focused laser beam (in combination with a spinning disk) is then used to write and erase (recrystallize) amorphous bits in a crystalline surrounding. Besides data storage in optical disks and in electrically controlled random access memories, PCMs have recently been used for switching the magnitude of Casimir-Lifshitz forces which can be promising for application in future micro/nanoelectromechanical devices.²

Scanning tunnelling microscopy and spectroscopy were employed to reveal the evolution of the band gap and the Fermi level as a function of the annealing temperature for PCMs.³ Nonetheless, and despite the extensive use of PCMs, little is known about the electrical properties of the amorphous-crystalline interface. This is important for down-scaling of electrically controlled non-volatile solid-state memories.⁴ In this case, the switching is done by Joule heating and the amorphous to crystalline transition shows a threshold switching event. Storage media with these so called phase random access memory (PRAM) cells have recently been introduced to the market, but still many questions regarding understanding and optimizing PCM properties and performance remain unanswered. When the data cells become smaller and smaller, the currents used to control these data cells during writing, erase, and reading also decrease. Contact resistances become increasingly important upon down scaling.⁵ Also, other electrical effects start to play a more dominant role during the switching process, implying that good understanding of all the electrical characteristics of the system is a prerequisite. This also holds for the amorphous-crystalline interface where the change of sur-

face potential, as this interface is crossed, appears to be important.

Indeed, since the amorphous phase is a semiconductor and the crystalline phase in general shows metallic like behaviour where free carriers have small mean free paths,⁶ the idea naturally emerges that a Schottky barrier might be present at the amorphous-crystalline interface giving rise to a local electric field. So far, this has not been measured directly and it will be the topic of the present paper using surface scanning potential microscopy (SSPM) and atomic force microscopy (AFM).

The PCM thin films used for our study were made by sputtering germanium (Ge) and antimony (Sb) onto a circular polycarbonate disc (1.4 mm thick). The thickness of the PCM films, having a Ge₇Sb₉₃ composition, was 200 nm, while a ~ 5.5 nm thick protective capping layer consisting of SiO₂-ZnS was deposited to protect the PCM film from oxidation and degradation. The amorphous PCM film was partially crystallized using heating. This yields, depending on the heating procedure, crystalline marks with different sizes/shapes (Fig. 1) and thus possibly different crystalline-amorphous interfaces. This is achieved by heating the sample with a relatively slow constant rate up to a certain temperature above the crystallization temperature of ~ 130 °C, but below ~ 155 °C, and then allow for isothermal crystallization, i.e., crystals nucleate with a certain incubation time (of less than a minute) *after* the isothermal temperature is reached. Following this procedure, the polycarbonate bottom substrate layer remained relatively stiff, because we remain below its glass transition temperature of ~ 155 °C. Above 155 °C, the crystallization process changes radically. In any case, the PCM films studied here have p-type conductivity with Ge acting as a kind of dopant.⁷

Furthermore, three types of samples were investigated, where different heating processes were used to achieve partial crystallization of the films (Fig. 1). These are, respectively, referred to as: C1 (Fig. 1(a); 20 °C/min up to a maximum temperature of 150 °C), C2 (Fig. 1(b); 10 °C/min up to a maximum temperature of 150 °C), and C3 (Fig. 1(c); 10 °C/min up to a maximum temperature of 140 °C). Figure 1 shows C1 and C2 samples that have large crystalline areas,

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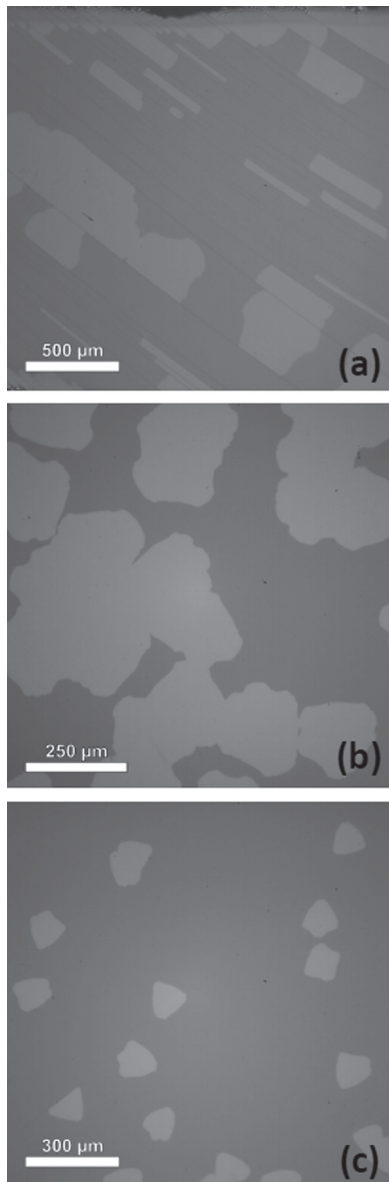


FIG. 1. Optical camera images of 200 nm thick partly crystalline $\text{Ge}_7\text{Sb}_{93}$ films: (a) C1 type, (b) C2 type, and (c) C3 type showing crystallites with a tendency to have a triangular shape.

while sample C3 contains smaller crystallites with triangular-like shape. The heating rate in case of Fig. 1(a) has been so high ($20^\circ\text{C}/\text{min}$) that the difference in thermal expansion between the substrate and the film resulted in parallel cracks in the PCM film. Despite the cracks, relatively straight amorphous-crystalline interfaces perpendicular to the cracks were formed, which are still very suitable for the present analysis. The atomic force microscope (AFM) setup used to perform the SSPM measurements (Figs. 2 and 3(a)) is a Multimode V (Bruker instruments) with a Nanoscope V controller. The AFM cantilevers/tips were made from Si and were n-type doped with Sb giving a resistivity of $\sim 0.01\text{--}0.025\ \Omega\text{-cm}$. The natural cantilever frequency was in the range $\sim 130\text{--}250\ \text{kHz}$ and the cantilever spring constant was $\sim 48\ \text{N/m}$ (determined with thermal tuning). Finally, the AFM/SSPM measurements were performed at ambient atmospheric conditions.

Figure 2 shows an AFM topography and the corresponding SSPM image of an area containing the amorphous-

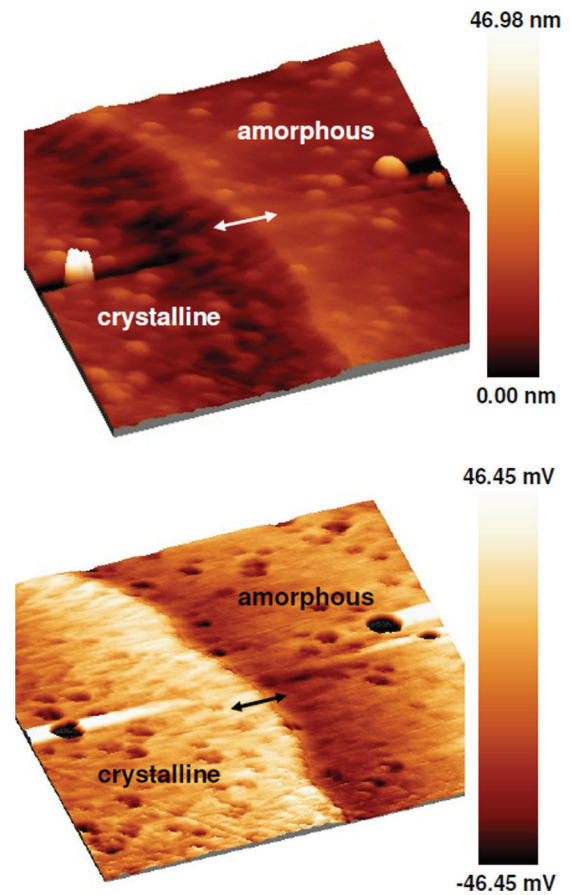


FIG. 2. (Color online) Top: AFM topography image for sample C2 across a crystalline/amorphous interface. Bottom: SSPM image. The scan size for both images was $5 \times 5\ \mu\text{m}^2$.

crystalline interface. Figure 3(a) shows the same image types, but now for a relatively small crystal that can be analysed as a whole embedded in the amorphous surrounding. The average height differences between the crystalline and amorphous areas, as deduced from the images in Figs. 2 and 3(a), is $\sim 10\text{--}15\ \text{nm}$, which is $\sim 5\%\text{--}7.5\%$ of the original amorphous layer thickness of $\sim 200\ \text{nm}$. This is in good agreement with findings for PCM materials where upon crystallization the crystalline area shrinks in thickness typically $\sim 6\%$.⁸ On the other hand, the SSPM image indicates the inverse behaviour for the surface potential yielding a higher potential over the crystalline area. Indeed, as the amorphous to crystalline transition area is crossed, the surface potential increases by $\Delta V \approx 60 \pm 30\ \text{mV}$ for all the samples studied. This potential change ΔV is, however, relatively constant along the same amorphous-crystalline transition area that has a width from topography analysis in the range $W_{\text{TOP}} \approx 300\text{--}1000\ \text{nm}$ for all the samples studied here (Fig. 4). The width of the surface potential change as we cross from the amorphous to crystalline area is slightly smaller of $W \approx 300\text{--}700\ \text{nm}$ (Fig. 4). Reduction of the resolution in SSPM is due to the transfer function defined by the derivatives of the capacitances between specimen and tip.⁹ Nevertheless, as Fig. 4 indicates, the amorphous-crystalline transition area is resolved in both AFM topography and SSPM mode. Transmission electron microscopy (TEM) analysis of the amorphous-crystalline interface for GeSb has shown that it is relatively sharp within a few atomic layers.

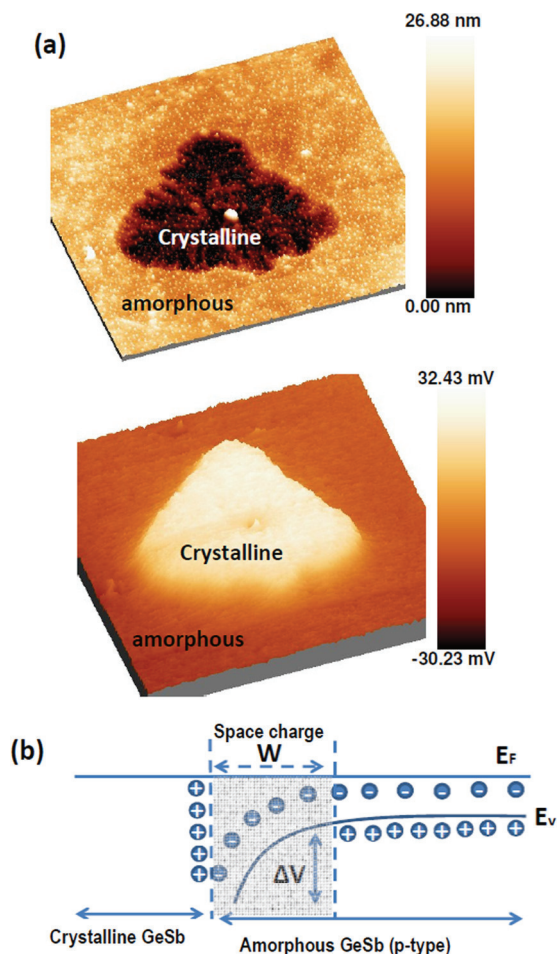


FIG. 3. (Color online) (a) Top: AFM topography image for sample C3 including a whole crystalline island. Bottom: SSPM image. The scan size for both images was $15 \times 15 \mu\text{m}^2$. (b) Schematic illustration of the formation of the Schottky barrier.

At the profiles, for example of Fig. 4, it is located at the bottom of the inclination where the crystalline phase commences.

A simple calculation of the potential barrier assuming that this is of Schottky type is as follows. When the two phases are in contact then the Fermi levels must be aligned

for the junction to be in equilibrium otherwise a current would flow. The amorphous phase behaves as a normal p-type semiconductor with the Fermi level lower than that of the crystalline phase, which behaves closely as a metal. Therefore, electrons flow from the crystalline to the amorphous phase. The migration of electrons causes a build-up of charge on both sides of the interface resulting in an electric field and a potential gradient in the semiconducting material. Due to this electric field, the majority carriers (holes in a p-type semiconductor) are pushed away from the interface resulting in an excess negative charge (caused by uncompensated charged acceptors) forming a depletion region of width W (Fig. 3(b)).¹⁰

Furthermore, a square charge density profile $\rho(x) = -qN\theta(W-x)$ (where $\theta(x)$ is the step function) is assumed within the semiconductor occupying the space $x > 0$ with N carriers, of charge q , per unit volume. This is valid when all the acceptors are ionized and the free charges have moved out of the interface region leaving behind the uncompensated ionized acceptors exactly up to a certain point W (Fig. 3(b)). The metal phase is assumed to occupy the $x < 0$ space. Then, the solution of the Poisson equation $d^2V/dx^2 = \rho(x)/\epsilon$, where ϵ is the semiconductor permittivity, with the boundary condition $V(x=W) = 0$ gives the potential expression $V(x) = qN(W-x)^2/2\epsilon$ for $0 \leq x \leq W$ ($V = 0$ for $x \geq W$ and $V = qNW^2/2\epsilon$ for $x \leq 0$).⁹ Thus, at the metal-semiconductor interface, $x = 0$, the Schottky potential height $\Delta V \approx qNW^2/2\epsilon$ is obtained.¹⁰ Assuming a typical dopant density of $N \approx 10^{21}/\text{m}^3$,⁸ $q = 1.6 \times 10^{-19}$ C, interface width $W \approx 400$ nm (obtained from SSPM images), and electric permittivity $\epsilon \approx 15\epsilon_0$ ($\epsilon_0 = 8.86 \times 10^{-12}$), an estimated Schottky barrier height of $\Delta V \approx 96$ mV is obtained. This is relatively close to the measured value of $\Delta V \approx 60 \pm 30$ mV.

Since the amorphous phase is a p-type semiconductor, the Fermi level is localized close to the valence band. As a result, the difference of the work functions, ignoring Fermi level matching and Schottky barrier formation, of the crystalline (ϕ_C) and amorphous (ϕ_A) phases would be $\phi_A - \phi_C \approx E_g$, where E_g is the band gap of the amorphous phase. Since for the eutectic GeSb phase $E_g \geq 0.4$ eV,⁷ the difference in work functions (ignoring Schottky barrier

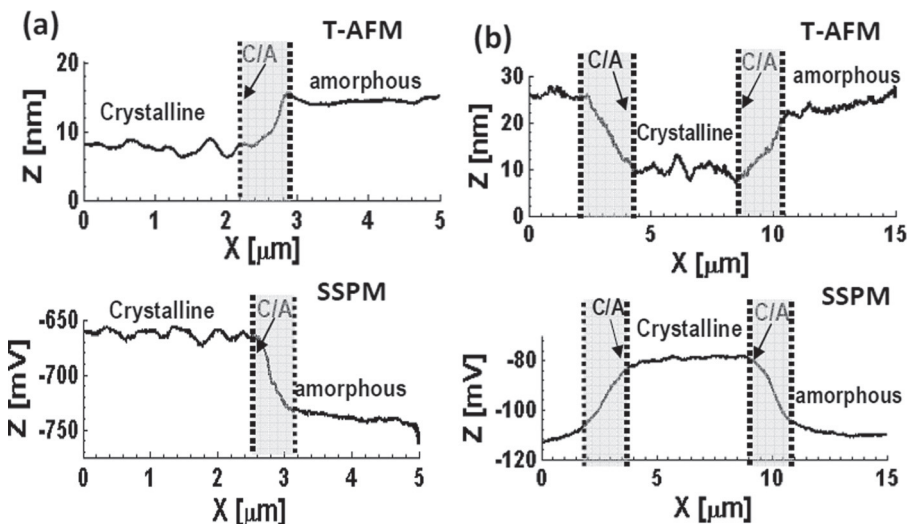


FIG. 4. Indicative profiles across the amorphous-crystalline areas in topography (T) AFM and SSPM mode: (a) sample C1 and (b) sample C3. In both cases, the crystalline-amorphous areas and the position of the C/A interface (arrow) are indicated in a qualitative sense.

formation) is much larger than the measured surface potential change ΔV ($\phi_A - \phi_C \gg \Delta V$). However, the Fermi level matching at the C/A interface associated with Schottky barrier formation indicates that ΔV arises mainly from the space charge region.

In conclusion, the surface potential changes across amorphous-crystalline interfaces in PCMs were investigated mainly by SSPM for the GeSb system. Analysis indicated a surface potential for the crystalline phase compared to the amorphous phase which is on average 60 mV higher and always larger than 30 mV. This change in surface potential is associated with the presence of a Schottky barrier at the amorphous/crystalline interface. The latter, if present, has to be taken carefully into account in the electrical characterization of PCMs.

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