Chapter 6

Electrical surface properties

Abstract. The electrical properties of amorphous-crystalline interfaces in phase-change materials are investigated in this chapter using 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 is also supported by quantitative Schottky model calculations.

6.1 Introduction

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 [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, phase-change materials 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 tunneling 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 phase-change materials. [3] Nonetheless, and despite the extensive use of phase-change materials, little is known about the electrical properties of the amorphous-crystalline interface. This is important for downscaling 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-change memory cells have recently been introduced to the market, but still many questions regarding understanding

and optimizing phase-change material 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 surface 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 behavior where free carriers have small mean free paths, [6] the idea nat-
urally 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 chapter using surface scanning potential microscopy (SSPM) and atomic
force microscopy (AFM).

6.2 Experimental

6.2.1 Samples

The phase-change thin films used for this chapter consist of a Ge$_7$Sb$_{93}$ 200 nm thin film on
a 1.3 mm polycarbonate substrate. The amorphous phase-change film was partially crystal-
lized by heating them on the hot plate. This yields, depending on the heating procedure, crys-
talline marks with different sizes and shapes (Fig. 6.1) 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 $\sim 130^\circ$C, but below
$\sim 155^\circ$C, and then allow for isothermal crystallization, i.e., crystals nucleate with a certain in-
cubation 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 $\sim 155^\circ$C. Above $155^\circ$C, the crystallization
process changes radically, as was shown in Fig. 1.1. In any case, the phase-change 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. 6.1). These are, respectively, re-
ferred to as: C1 (Fig. 6.1a; 20°C min$^{-1}$ up to a maximum temperature of 150°C), C2 (Fig.
6.1b; 10°C min$^{-1}$ up to a maximum temperature of 150°C), and C3 (Fig. 6.1c; 10°C min$^{-1}$ up
to a maximum temperature of 140°C). Figure 6.1 shows C1 and C2 samples that have large
crystalline areas, while sample C3 contains smaller crystallites with triangular-like shape. The
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Figure 6.1 | Optical camera images of 200 nm thick partly crystalline Ge$_7$Sb$_{93}$ films: a C1 type, b C2 type, and c C3 type showing crystallites with a tendency to have a triangular shape.

heating rate in case of Fig. 6.1a has been so high (20 °C min$^{-1}$) that the difference in thermal expansion between the substrate and the film resulted in parallel cracks in the phase-change film. Despite the cracks, relatively straight amorphous-crystalline interfaces perpendicular to the cracks were formed, which are still very suitable for the present analysis.

6.2.2 Surface measurements

The atomic force microscope (AFM) setup used to perform the SSPM measurements (Figs. 6.2 and 6.3) 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 ∼0.01–0.025 Ω cm. The natural cantilever frequency was in the range ∼130–250 kHz and the cantilever spring constant was ∼48 N m$^{-1}$ (determined with thermal tuning). Finally, the AFM/SSPM measurements were performed at ambient atmospheric conditions.

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Figure 6.2 shows an AFM topography and the corresponding SSPM image of an area containing the amorphous-crystalline interface. Figure 6.3 shows the same image types, but now for a relatively small crystal that can be analyzed 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. 6.2 and 6.3, is 10–15 nm, which is 5 %–7.5 % of the original amorphous layer thickness of 200 nm. This is in good agreement with findings for phase-change materials where upon crystallization the crystalline area shrinks in thickness typically 6 %. [8] On the
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Figure 6.2 | a AFM topography image for sample C2 across a crystalline/amorphous interface. b SSPM image. The scan size for both images was 5 µm × 5 µm.

Figure 6.3 | a AFM topography image for sample C3 including a whole crystalline island. b SSPM image. The scan size for both images was 15 µm × 15 µm.

other hand, the SSPM image indicates the inverse behavior 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 $\Delta V \approx 60 \pm 30$ mV for all the samples studied. This potential change $\Delta V$ is, however, relatively constant along the same amorphous-crystalline transition area that has a width from topography analysis in the range $W_{\text{TOP}} \approx 300–1000$ nm for all the samples studied here (Fig. 6.4). The width of the surface potential change as we cross from the amorphous to crystalline area is slightly smaller of $W \approx 300–700$ nm (Fig. 6.4). Reduction of the resolution in SSPM is
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Figure 6.4 | 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 (grayed area) are indicated in a qualitative sense.

... due to the transfer function defined by the derivatives of the capacitances between specimen and tip. [9] Nevertheless, as Fig. 6.4 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. At the profiles, for example of Fig. 6.4, 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. 6.5). [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. 6.5). The metal phase is assumed to occupy the \( x < 0 \) space. Then, the solution of the Poisson equation \( \frac{d^2 V}{dx^2} = \rho(x)/\epsilon \), where \( \epsilon \) 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 \( N \approx 1 \times 10^{21} \) 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 (\( \phi_C \)) and amorphous (\( \phi_A \)) 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 formation) is much larger than the measured surface potential change \( \Delta V \approx 96 \) mV. However, the Fermi level matching at the C/A interface associated with Schottky barrier formation indicates that \( \Delta V \) arises mainly from the space charge region.

### 6.4 Conclusions

The surface potential changes across amorphous-crystalline interfaces in phase-change materials 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 phase-change materials.
References


