Nanoscale mechanically induced structural and electrical changes in Ge$_2$Sb$_2$Te$_5$ films

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We demonstrate that the microstructure and electrical properties of Ge$_2$Sb$_2$Te$_5$ films can be changed by a nanoscale mechanical process. Nanoscratching is used to define modified areas onto an as-deposited crystalline Ge$_2$Sb$_2$Te$_5$ film. Scanning tunneling microscopy measurements show that the modified areas have a very low electrical conductivity. Micro-Raman measurements indicate that the mechanically induced microstructural changes are consistent with a phase transformation from crystalline to amorphous, which can be reversed by laser irradiation. © 2012 American Institute of Physics. [doi:10.1063/1.3673592]

Chalcogenide compounds, such as Ge$_2$Sb$_2$Te$_5$, are attracting great interest due to their optoelectronic properties and to their applications in data storage devices. In optical phase change systems, such as DVD-RAM, chalcogenide films are written and erased by optical heating, while information is read by a weaker light source. In the emerging technology of probe-based storage systems where, similarly to the PCRAM devices are based on the reversible phase change process occurring in the active film and the consequent change of optical contrast and electrical conductivity. Despite the long-established technological applications of chalcogenide films in optical data storage devices and the high level reached in the development of PCRAM, the phase change process of such compounds is still the object of intense theoretical and experimental investigations. These include the study of the atomic bonds rearrangement upon phase transition, using, e.g., Raman scattering spectroscopy measurements, which are very sensitive to the lattice vibrations that reflect the local symmetry of the material, and the investigation on the structural changes induced by hydrostatic pressure. On the other hand, alternative processes for the writing and reading of information that would allow higher storage density and overcome, for instance, the limits imposed by diffraction of laser impulse in optical storage devices are sought. Among these attempts is the investigation on scanning probe based storage systems where, similarly to the PCRAM cells, writing of bits by conductive probes involves an electrothermal process in which Joule heating provides the energy required for film crystallization or amorphization.

In this work we report that microstructural and conductivity change of crystalline Ge$_2$Sb$_2$Te$_5$ films in the nanoscale range can also be obtained by a mechanical process via nanoscratching. In analogy with laser or electrical writing, the mechanically modified film regions have much lower conductivity than unmodified regions and show microstructural features that are consistent with the amorphous state of the Ge$_2$Sb$_2$Te$_5$ alloy. Moreover, as in the optical erase process, the microstructure of the film can be reversed to its original state by laser irradiation.

Ge$_2$Sb$_2$Te$_5$ films with face-centered-cubic (f.c.c.) polycrystalline structure, as verified by x-ray diffraction (XRD) measurements, and thicknesses in the range from 70 to 3500 nm were deposited by magnetron sputtering in a ~2 mTorr Ar atmosphere and using a power of ~0.5 kW from a single Ge$_2$Sb$_2$Te$_5$ target on n-doped Si (100) substrates, kept at 130 °C.

Nanoscratching was performed with an Hysitron® UBI nanoindenter, mounting a Berkovich diamond tip, by simultaneously applying a fixed constant force in the range of 100–300 μN along the z direction and scanning the tip laterally in the x-y directions at a rate of 130 μm/s. The morphology of the scratched areas was investigated with a Nanotec® Cervantes atomic force microscope (AFM) operated in tapping mode and a Nanotec® scanning tunneling microscope (STM) mounting a Pt/Ir tip, which was also used to measure the current-voltage (1-V) characteristics of the unmodified and scratched areas. The microstructural characterization of the scratched and unmodified areas was done at room temperature with a Horiba Jobin-Yvon® LabRAM micro-Raman spectrometer equipped with a charge-coupled device detector and an unpolarised 785 nm probe laser, using a 100× magnification objective and a 100 μm pinhole. The laser intensity on the sample and the acquisition time were adjusted to a level that produced no discernible change in the sample spectrum during the characterization measurements. The same micro-Raman system was used to irradiate the sample with higher laser intensity (~3 mW/μm² for ~40 s). The changes induced by the laser in the higher intensity condition were then measured in the low intensity laser mode.

Using the nanoindenter, several parallel scratches were created one next to the other on the Ge$_2$Sb$_2$Te$_5$ films, defining square patterns of ~60 μm × 60 μm of modified material like the one reported in Fig. 1. The spacing between adjacent scratches was kept below the scratch width (which was in the range of 200–500 nm depending on the load used), so that scratches overlap and no areas within the square pattern are left unmodified. Figure 2(a) reports the AFM topographic image of

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a region near the edge of one of these patterns, where the morphologies of both unmodified (original layer) and scratched surfaces are visible. The AFM height profile along a line crossing both areas is shown in Fig. 2(c). Figure 2(b) shows the STM image of an equivalent region on the same square pattern scanned applying a voltage bias of 0.15 V to the probe against the substrate. While the topography of the unmodified area is similar to the one obtained by AFM, a constant null signal is obtained by STM inside the modified area due to the insulating electrical behavior of this region. The absence of current above the sensitivity limit of our STM (~3 pA), even with the probe in physical contact with the substrate, implies an equivalent contact resistance of \( \geq 50 \text{G} \Omega \) at 0.15 V bias for the modified Ge\(_2\)Sb\(_2\)Te\(_5\) area. For comparison, the electrical properties of the original layer are shown in Fig. 2(d), where the I-V curve measured by STM on such area is reported.

Figure 3 shows the micro-Raman spectra recorded in the low intensity laser mode on the unmodified and scratched areas respectively. The relative increase of the peak at \( \sim 150 \text{ cm}^{-1} \) with respect to the peak at \( \sim 105 \text{ cm}^{-1} \) observed on the modified areas has been reported in numerous studies as the main Raman feature of the amorphous phase with respect to the crystalline phase of Ge\(_2\)Sb\(_2\)Te\(_5\).\(^{3-6,10}\) The additional peak appearing at \( \sim 120 \text{ cm}^{-1} \) on the modified areas has also previously been associated with amorphous Ge\(_2\)Sb\(_2\)Te\(_5\).\(^{4,6}\) Similar differences in the Raman spectra between unmodified and modified areas were observed on 70 nm and 2000 nm thick Ge\(_2\)Sb\(_2\)Te\(_5\) films. Moreover, the Raman spectrum obtained on the modified area after exposure to the higher laser intensity, also shown in Fig. 3, indicates a reversal to a microstructure similar to the original crystalline phase, in agreement with a laser induced crystallization of the amorphous phase. It can therefore be concluded that nanoscratching induces an amorphization of Ge\(_2\)Sb\(_2\)Te\(_5\) and that this phase can be reversed to the crystalline state by laser irradiation. Given that the interaction volume of the scratch tip should have a radius close to half of the scratch width, a thickness of \( \sim 230 \text{ nm} \) for the modified layer could be estimated when a 250 \( \mu \text{N} \) load is used.
Phase change phenomena have been widely reported during nanoindentation and nanoscratching of crystalline Si and GaAs\textsuperscript{16–20}, and are explained with the transition from the f.c.c. Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} films to the high pressure crystalline phases to the amorphization of scratched Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (b) and its laser induced recrystallization (c). In the case of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5}, it is known that the as-deposited phase undergoes subsequent transitions under hydrostatic pressures of several gigapascals.\textsuperscript{8} In particular the amorphization of f.c.c. Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} under hydrostatic pressure above \textasciitilde 10 GPa has been demonstrated.\textsuperscript{7} A rough estimate of the pressure under the indenter for the fully plastic regime of deformation is given by the hardness of the material, which was measured under the indenter for the fully plastic regime of deformation and the applied load, the definition of nanometric features on Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} films should be possible using, for instance, sharper tips and/or an AFM instead of a nanoindenter. Our findings might help clarifying the mechanisms of pressure induced phase transformation of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5}. They might also find applications within the efforts of developing scanning probe based memory devices using chalcogenides films.

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\begin{thebibliography}{99}
\bibitem{15} See supplementary material at http://dx.doi.org/10.1063/1.3673592 XRD patterns of as-deposited Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} films.
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