Nanoscale mechanically induced structural and electrical changes in $Ge_2Sb_2Te_5$ films

R. Cecchini,[a)] J. J. Benítez, J. C. Sánchez-López, and A. Fernández
Instituto de Ciencia de Materiales de Sevilla, CSIC-Universidad de Sevilla, Avenida Américo Vespucio 49, 41092 -Seville, Spain

(Received 13 September 2011; accepted 29 November 2011; published online 3 January 2012)

We demonstrate that the microstructure and electrical properties of $Ge_2Sb_2Te_5$ films can be changed by a nanoscale mechanical process. Nanoscratching is used to define modified areas onto an as-deposited crystalline $Ge_2Sb_2Te_5$ 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 $Ge_2Sb_2Te_5$, 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.[1] In the emerging technology of phase change random access memories (PCRAM), data are written and read by high and low current impulses, respectively.[2] Both optical and 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,[3–6] and the investigation on the structural changes induced by hydrostatic pressure.[7,8] 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.[9–14]

In this work we report that microstructural and conductivity change of crystalline $Ge_2Sb_2Te_5$ 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 $Ge_2Sb_2Te_5$ alloy. Moreover, as in the optical erase process, the microstructure of the film can be reversed to its original state by laser irradiation.

$Ge_2Sb_2Te_5$ films with face-centered-cubic (f.c.c.) polycrystalline structure, as verified by x-ray diffraction (XRD) measurements,[15] and thicknesses in the range from 70 to 3500 nm were deposited by magnetron sputtering in a $\sim$2 mTorr Ar atmosphere and using a power of $\sim$0.5 kW from a single $Ge_2Sb_2Te_5$ 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 (I-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 ($\sim$3 mW/μm^2 for $\sim$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 $Ge_2Sb_2Te_5$ films, defining square patterns of $\sim$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

[a)]Electronic mail: raimondo.cecchini@tiscali.it.

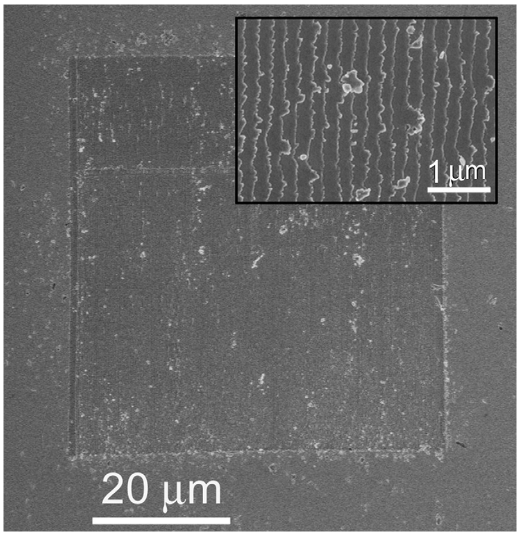

FIG. 1. SEM image of a ~60 μm × 60 μm square pattern obtained by nanoscratching a 2000 nm thick crystalline $Ge_2Sb_2Te_5$ film with a force of 300 μN. In the inset a higher magnification image of the scratches. Scratches have a width of ~500 nm and are separated by 250 nm one from the other, so that no area within the square pattern is left unmodified.

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 GΩ at 0.15 V bias for the modified $Ge_2Sb_2Te_5$ 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 ~150 cm^{-1} with respect to the peak at ~105 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 $Ge_2Sb_2Te_5$.[3–6,10] The additional peak appearing at ~120 cm^{-1} on the modified areas has also previously been associated with amorphous $Ge_2Sb_2Te_5$.[4,6] Similar differences in the Raman spectra between unmodified and modified areas were observed on 70 nm and 2000 nm thick $Ge_2Sb_2Te_5$ 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 $Ge_2Sb_2Te_5$ and that this phase can be reversed to the crystalline state by laser irradiation. The estimation of the thickness of the mechanically amorphized $Ge_2Sb_2Te_5$ layer is not straightforward. Given that the interaction volume of the scratch tip should have a radius close to half of the scratch width, a thickness of ~230 nm for the modified layer could be estimated when a 250 μN load is used.

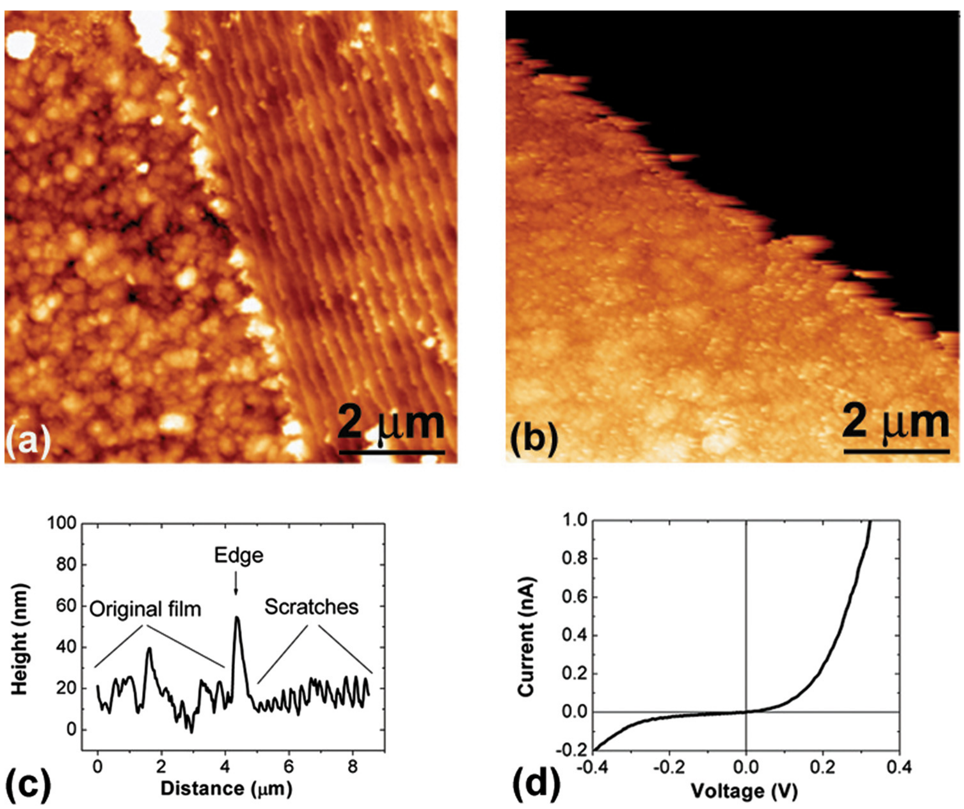

FIG. 2. (Color online) (a) AFM topographic image of a region near the edge of a scratched pattern (scratching force = 250 μN) on a 3500 nm thick $Ge_2Sb_2Te_5$ film; (b) STM constant current image over an equivalent area of the same pattern obtained applying a positive bias voltage of 0.15 V to the probe and a 0.6 nA set point; (c) AFM height profile along a line crossing the original and scratched areas; (d) I-V curve measured by STM on the original layer. Instead, a constant null current value is obtained inside the modified area (dark region in (b)) indicating the insulating properties of scratched $Ge_2Sb_2Te_5$.

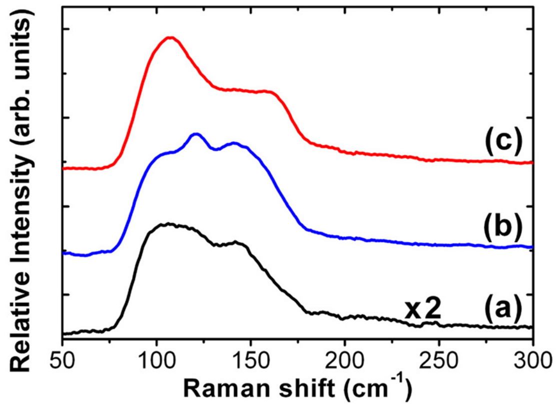

FIG. 3. (Color online) Micro-Raman spectra recorded on (a) an as-deposited crystalline $Ge_2Sb_2Te_5$ area (intensity multiplied by 2), (b) a scratched pattern (scratching force = 250 μN) and (c) on a region of the same scratched area after irradiation in the higher laser intensity mode. The position of the Raman peaks and their relative intensities indicate an amorphization of scratched $Ge_2Sb_2Te_5$ (b) and its laser induced recrystallization (c).

Phase change phenomena have been widely reported during nanoindentation and nanoscratching of crystalline Si and GaAs[16–20] and are explained with the transition from the original structure to high pressure phases under the effect of the tip during loading. Certain conditions of unloading, e.g., fast unloading, might not give enough time for lattice reconstruction into the low pressure crystalline phases to the deformed material, resulting in the formation of an amorphous mark in the indented or scratched regions.[16,17] In the case of $Ge_2Sb_2Te_5$, it is known that the as-deposited phase undergoes subsequent transitions under hydrostatic pressures of several gigapascals.[8] In particular the amorphization of f.c.c. $Ge_2Sb_2Te_5$ under hydrostatic pressure above $\sim$10 GPa has been demonstrated.[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 by nanoindentation to be $\sim$3 GPa for the presently studied $Ge_2Sb_2Te_5$ films. This value is much lower than the value required for phase transition under hydrostatic pressure conditions. It is therefore unlikely that the same description used to explain the phase transformation during indentation and nanoscratching of, e.g., Si, with transition of the microstructure through high pressure phases, can be applied to the present case. On the other hand, it seems plausible to refer the observed microstructural changes of crystalline $Ge_2Sb_2Te_5$ to the disruption of order occurring in the material during plastic deformation induced by scratching. Surface modifications, including amorphization, induced by grinding and wear processes have been observed on metallic alloys and referred to the severe plastic deformation mechanism.[21,22] Further investigation about the effect of the scratching parameters, e.g., the scratching speed (and hence of the strain rate[23]) and the applied load, on the above described changes could help explaining the mechanisms involved in the phase transformation.

In summary, we have demonstrated that a modification of the microstructural and electrical properties of polycrystalline f.c.c. $Ge_2Sb_2Te_5$ films can be obtained by a nanoscale mechanical process. These changes and the observed reversal of the microstructure to its original state upon laser irradiation are consistent with an amorphization of the film in the scratched regions. As both vertical and lateral size of modified material should scale with the probe size dimension and the applied load, the definition of nanometric features on $Ge_2Sb_2Te_5$ 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 $Ge_2Sb_2Te_5$. They might also find applications within the efforts of developing scanning probe based memory devices using chalcogenides films.

This research has been supported by CSIC (NANO-CONTROL 201060E102), Spanish Ministry MICINN (Consolider FUNCOAT CSD2008-00023), and Junta de Andalucia (TEP217). The authors also thank the Metallurgy group of Department of Mechanical Engineering of Università Politecnica delle Marche (Ancona, Italy) for providing access to its nanoindentation/nanoscratch instrument and J.C. Gonzalez for his help with the analysis of the micro-Raman measurements.

[1]T. Ohta, K. Nishiuchi, K. Narumi, Y. Kitaoka, H. Ishibashi, N. Yamada, and T. Kozaki, Jpn. J. Appl. Phys. **39**, 770 (2000).
[2]A. Pirovano, F. Pellizzer, I. Tortorelli, A. Riganó, R. Harrigan, M. Magistretti, P. Petruzza, E. Varesi, A. Redaelli, D. Erbetta, T. Marangon, F. Bedeschi, R. Fackenthal, G. Atwood, and R. Bez, Solid-State Electron. **52**, 1467 (2008).
[3]A. V. Kobolov, P. Fons, A. Frenkel, A. L. Ankudinov, J. Tominaga, and T. Uruga, Nature Mater. **3**, 703 (2004).
[4]R. De Bastiani, A. M. Piro, M. G. Grimaldi, E. Rimini, G. A. Baratta, and G. Strazzulla, Appl. Phys. Lett. **92**, 241925 (2008).
[5]M. Krbal, A. V. Kolobov, P. Fons, J. Tominaga, S. R. Elliott, J. Hegedus, and T. Uruga, Phys. Rev. B **83**, 054203 (2011).
[6]P. Němec, A. Moreac, V. Nazabal, M. Pavlišta, J. Přikryl, and M. Frumar, J. Appl. Phys. **106**, 103509 (2009).
[7]A.V. Kolobov, J. Haines, A. Pradel, M. Ribes, P. Fons, J. Tominaga, Y. Katayama, T. Hammouda, and T. Uruga, Phys. Rev. Lett. **97**, 035701 (2006).
[8]M. Krbal, A. V. Kolobov, J. Haines, A. Pradel, M. Ribes, P. Fons, J. Tominaga, C. Levelut, R. Le Parc, and M. Hanfland, Appl. Phys. Lett. **93**, 031918 (2008).
[9]H. Kado and T. Tohda, Appl. Phys. Lett. **66**, 2961 (1995).
[10]H. Satoh, K. Sugawara, and K. Tanaka, J. Appl. Phys. **99**, 024306 (2006).
[11]K. Tanaka, J. Non-Cryst. Solids **353**, 1899 (2007).
[12]K. Sugawara, T. Gotoh, and K. Tanaka, J. Non-Cryst. Solids **326–327**, 37 (2003).
[13]H. J. Kim, S. K. Choi, S. H. Kang, and K. H. Oh, Appl. Phys. Lett. **90**, 083103 (2007).
[14]C. D. Wright, P. Shah, Lei Wang, M. M. Aziz, A. Sebastian, and H. Pozidis, Appl. Phys. Lett. **97**, 173104 (2010).
[15]See supplementary material at http://dx.doi.org/10.1063/1.3673592 XRD patterns of as-deposited $Ge_2Sb_2Te_5$ films.
[16]V. Domnich, Y. Gogotsi, and S. Dub, Appl. Phys. Lett. **76**, 2214 (2000).
[17]J. Jang, M. J. Lance, S. Wen, T. Y. Tsui, and G. M. Pharr, Acta Mater. **53**, 1759 (2005).
[18]S. Ruffell, J. E. Bradby, and J. S. Williams, Appl. Phys. Lett. **89**, 091919 (2006).
[19]S. T. Ho, Y. H. Chang, and H. N. Lin, J. Appl. Phys. **96**, 3562 (2004).
[20]Z. C. Li, L. Liu, X. Wu, L. L. He, and Y. B. Xu, Mater. Sci. Eng. A **337**, 21 (2002).
[21]X. Y. Li and K. N. Tandon, Acta Mater. **44**, 3611 (1996).
[22]H.W. Jin, C. G. Park, and M. C. Kim, Surf. Coat. Technol. **113**, 103 (1999).
[23]K. Wasmer, M. Parlinska-Wojtan, R. Gassilloud, C. Pouvreau, J. Tharian, and J. Micher, Appl. Phys. Lett. **90**, 031902 (2007).