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Femtosecond laser-induced nanostructure formation in Sb_2Te_3

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We report femtosecond laser-induced nanotracks in highly absorbing Sb_2Te_3. Groups of nanotracks are observed with widths ~50 nm and periodicity ~130 nm, their area of coverage extending with the increase of laser fluence. We demonstrate that under a narrow range of laser fluences and laser irradiation times, long highly aligned nanotracks can be formed in Sb_2Te_3. The results suggest a promising avenue for laser nanostructuring of chalcogenide thermoelectrics, with implications for high efficiency thermoelectric energy conversion. © *2011 American Institute of Physics*. [doi:10.1063/1.3634014]

Antimony telluride (Sb_2Te_3) is one of the most widely used materials for thermoelectric applications.[1] Presently, it is of interest to study the thermoelectric properties of low dimensional structures such as thin films, wires, and quantum dots. These structures have been predicted[2,3] to have significantly higher energy conversion efficiency than bulk forms of the material on account of energy filtering, quantum confinement, and enhanced phonon scattering on multiple boundaries. Recent measurements on Sb_2Te_3 nanowires suggest that thermoelectric power enhancement may be possible at the smallest wire diameters.[4] In addition to its attractive thermoelectric properties, the band structure of Sb_2Te_3 makes it a promising candidate material for realization of a topological insulator,[5] which is characterized by conductive states at the surface and insulating states in the bulk. Of particular interest are one-dimensional nanostructures that provide a means to tune the surface-to-volume ratio and thereby enhance the contribution of exotic surface states.[6] Therefore, the preparation of nanostructures in Sb_2Te_3 has wide potential applications.

Among the various efforts to prepare nanostructures, femtosecond laser-induced modification has attracted considerable interest.[7–16] In particular, structures with periods significantly smaller than the laser wavelength are observed predominantly in transparent and semi-transparent materials,[10–16] for which the imaginary part κ of the complex refractive index $\tilde{n} = n + i\kappa$ is negligible. For example, a well studied transparent material is diamond,[17–20] in which recent efforts have clearly demonstrated highly aligned and highly uniform nanostructures written with a femtosecond laser approach.[20] On the other hand, similar observations are rarely reported for absorptive materials with κ comparable to n. As a result, femtosecond laser-induced nanostructure formation has remained elusive for certain technologically important materials such as Sb_2Te_3, a narrow bandgap semiconductor which is highly absorbing in the visible and near-infrared spectral regions.[21]

In this letter, we report on the formation of femtosecond laser-induced nanotracks on both bulk and epitaxial thin film forms of Sb_2Te_3. The nanotracks have widths ~50 nm and periods $\Lambda \sim 130$ nm, less than 10% of the laser wavelength, λ. Our results describing the dependence of Sb_2Te_3 material modification on both the laser fluence and irradiation time highlight the formation of such nanostructures in strongly absorbing material.

The experiments were performed on a bulk Sb_2Te_3 sample and several Sb_2Te_3 thin films grown on Al_2O_3 (sapphire) substrates by molecular beam epitaxy (MBE). A fiber laser provided 100 femtosecond pulses at a repetition rate of 100 MHz, with a wavelength of 1580 nm. The linearly polarized laser pulses were focused at normal incidence onto the surface of the film with a focal spot diameter of ~3 μm. The laser fluence incident on the film surface could be varied from approximately 3 mJ/cm^2 to 6 mJ/cm^2 by using a half-wave plate followed by a polarizer. The samples were mounted on an xyz-translation stage that was scanned at different speeds from 1 μm/s to 500 μm/s in the direction perpendicular to the laser propagation. This allowed the laser to scan across the sample as it irradiated the surface. The laser-writing process was carried out under ambient conditions. The laser-scanned regions were then examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Figure 1 shows an SEM image of laser-induced nanostructure formation on a 200 nm Sb_2Te_3 film. The surface roughness of the film, defined as the arithmetical average of the surface profile, R_a, is ~5 nm. The irradiation fluence and scan speed were 6.3 mJ/cm^2 and 10 μm/s, respectively. Four highly aligned nanotracks are clearly visible in the irradiated region, with widths in the range of 45-80 nm and an average spacing, Λ, of 130 ± 10 nm. The observed spacing is consistent with an estimate based on the lateral interference condition[16] $\Lambda = \lambda/2n = 131.7$ nm ($\lambda = 1580$ nm and $n \approx 6$).[21] AFM measurements reveal that the peak-to-valley amplitude of the nanotracks is approximately 50 nm, which is close to the laser's penetration depth in Sb_2Te_3 ($\delta = \lambda/4\pi\kappa \approx 60$ nm). Also, on bulk Sb_2Te_3, we observed more than ten highly aligned tracks with widths of approximately 40 nm and lengths of at least 19 μm. This is a clear indication that we

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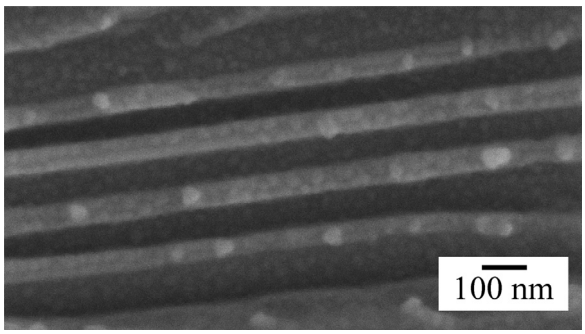

FIG. 1. SEM image of nanotracks on a 200 nm Sb_2Te_3 film after irradiation by a 1580 nm femtosecond laser with a fluence of 6.3 mJ/cm^2 and a scan speed of 10 μm/s.

are able to form nanotracks on both bulk and thin film forms of Sb_2Te_3.

In order to study the dependence of nanostructure formation and morphology on laser fluence, we irradiated three regions at a speed of 10 μm/s on another 200 nm Sb_2Te_3 film with roughness $R_a \sim 23$ nm, each with a different fluence: 3.9 mJ/cm^2, 5.2 mJ/cm^2, and 6.3 mJ/cm^2 (Fig. 2). For all three regions, groups of nanotracks were observed to develop with a 1.5 ± 0.1 μm periodicity matching that of the laser wavelength. These nanotrack groups were separated by smoother regions which appear to be annealed. As the fluence increased, the areas covered by the nanotracks expanded into the annealed regions and eventually covered the entire irradiated area; however, over the range of fluences tested, we observed no change in the period of the nanotracks themselves ($\sim$130 nm). Furthermore, the fluence threshold for nanotrack formation in this sample appears to be smaller than that of the smoother sample shown in Fig. 1.

We analyze the periodic appearance of nanotrack groups and its dependence on laser fluence in terms of the following processes: the interference between the normal-incidence laser beam and the surface-scattered electromagnetic wave creates a periodic variation of laser intensity along the sample's surface with a period equal to the laser's wavelength.[22,23] Near the nodes of the interference pattern, the low intensity laser irradiation causes mild annealing of the film surface, while near the antinodes of the interference pattern, the high laser intensity leads to periodic removal of material from the surface of the film. As the laser fluence grows from 3.9 mJ/cm^2 to 6.3 mJ/cm^2, the amplitude of the interference standing wave increases, thereby expanding the areas around the antinodes in which the laser intensity exceeds the threshold for material removal. Consequently, the nanostructure formation extends outwards into the annealed areas as the laser fluence increases (see Fig. 2).

The nanostructure morphology depends not only on laser fluence but also on the laser irradiation time, which is controlled by the scan speed. Fig. 3 shows two regions on the same film as in Fig. 1 irradiated by a laser fluence of 6.3 mJ/cm^2 at two different scan speeds: 1 μm/s and 10 μm/s. At 1 μm/s, the irradiated region is dominated by quasi-ordered nanostructures. As the speed increases to 10 μm/s and the corresponding irradiation time decreases by a factor of 10, the irradiated region becomes covered with highly ordered and continuous nanotracks with spacing comparable to their width.

The substantial change in nanotrack morphology with laser irradiation time may be related to the complex interaction processes between the ultrafast laser and the film, which include not only thermal mechanisms but also electronic effects.[24] We suggest that for the slower speed (longer irradiation time) of 1 μm/s, the large amount of accumulated heat[25] melts the surface of Sb_2Te_3, and the quasi-ordered nanostructures of Fig. 3(a) originate from a liquid state. For the faster speed of 10 μm/s (shorter irradiation time), the surface of Sb_2Te_3 is not hot enough to melt, and the nanotrack formation results from the modification of a solid phase. In addition, results from energy dispersive x-ray spectroscopy show that the laser-modified regions in Fig. 3(b) retain the Sb_2Te_3 stoichiometry. Optical phonon spectroscopy also indicates that Sb_2Te_3 decomposition observed previously[26] is insignificant at such high scan speeds and short irradiation times. This is a promising result for the fabrication of stoichiometric Sb_2Te_3 nanowires.

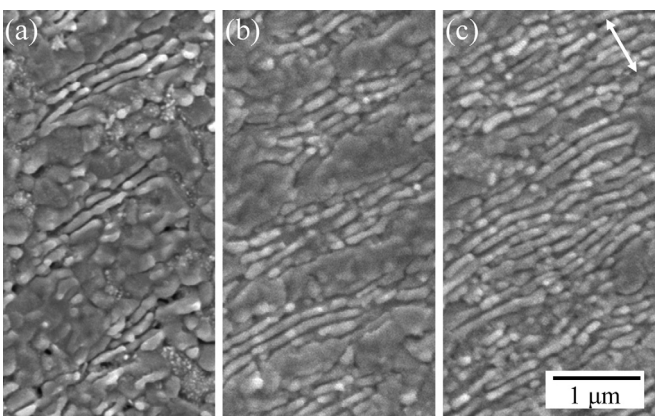

FIG. 2. SEM images of nanotracks on a 200 nm Sb_2Te_3 film after irradiation by a 1580 nm femtosecond laser with a scan speed of 10 μm/s and fluences of (a) 3.9 mJ/cm^2, (b) 5.2 mJ/cm^2, and (c) 6.3 mJ/cm^2. The arrow indicates the plane of laser polarization. Note that as the laser fluence increases, the areas covered by nanotracks extend into the annealed areas.

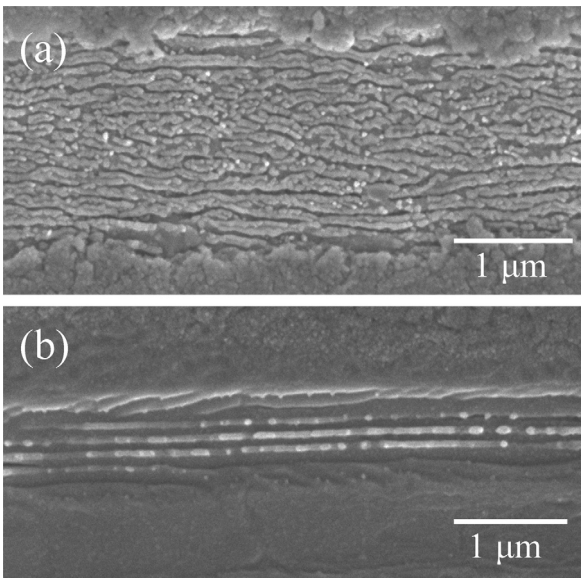

FIG. 3. SEM images of nanotracks on a 200 nm Sb_2Te_3 film after irradiation by a 1580 nm femtosecond laser with a fluence of 6.3 mJ/cm^2 and scan speeds of (a) 1 μm/s and (b) 10 μm/s.

The studies of laser-induced nanostructures presented here have important implications for controlling the physical properties of Sb_2Te_3. In particular, one would expect significant changes in thermal and electronic transport to arise from the formation of nanostructures. Indeed, using time-domain thermoreflectance techniques[27] we have measured reductions in the thermal conductivity of laser-modified regions of Sb_2Te_3 thin films compared to unmodified regions. These results, which are the subject of ongoing investigations to be reported in a separate publication, demonstrate one example of the potential benefits of femtosecond laser-induced nanostructuring for improving a material's thermoelectric efficiency.

In conclusion, we have observed femtosecond laser-induced nanostructures in Sb_2Te_3 in the strongly absorbing regime. This observation highlights the encouraging possibility of their formation not only in transparent dielectrics but also in strongly absorbing narrow-gap materials that are important to future technologies. Most importantly, our measurements have revealed the existence of a regime in which ordered nanotracks emerge under ultrafast laser irradiation, not simply as a result of melting and recrystallization. Finally, we note that similar nanostructure formation has been observed in other absorptive layered materials typified by van der Waals bonding.[18] It is an interesting open question what role the weakly bonded layers in Sb_2Te_3 play during laser modification. Our work serves as an important step toward controlled formation of nanostructures in Sb_2Te_3. We expect that similar laser-induced nanostructure formation may also occur in other tetradymite-type materials, which form a major branch of current thermoelectric technology.

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