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Optical properties of Cr-doped Sb_2Te thin films during ultrafast crystallization processes

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ABSTRACT

The crystallization process of Cr-doped Sb_2Te thin films induced by repeated femtosecond laser pulses was studied systematically. The threshold effects and corresponding mechanism were comprehensively analyzed by real-time reflectivity measurements, optical microscopic imaging, and Raman scattering spectra. It was found that by doping the appropriate content of Cr into Sb_2Te thin films, improved optical-thermal properties could be obtained, even in ultrafast crystallization processes.

1. Introduction

Phase-change materials have been used as recording media for commercialized data storage products since the launching of rewritable optical disks in the 1980s. Phase-change memory (PCM) is becoming a promising candidate for the so-called “universal memory” due to its high scalability, nonvolatile nature, low power consumption, high read/write speeds, and long service life [1,2,3]. During the development process, various phase-change materials were examined, and some classic recording materials used in phase-change optical disks were found to perform well in terms of contrast, speed, and stability for PCM applications.

On the ternary phase diagram of Ge, Te, and Sb, the tie line between GeTe and Sb_2Te_3, the region around Sb_2Te as well as the area around Sb are well known to form the three most important classes of phase-change materials discovered thus far. Unlike many Te-rich chalcogenide materials, such as Sb_2Te_3 and $Ge_2Sb_2Te_5$, Sb-rich materials, such as Sb_2Te (or $Sb_{70}Te_{30}$ with a very similar composition) and AgInSbTe, are growth-dominant (or even nucleation-free) materials, which are often considered to be suitable for high-speed erasing (crystallization) and overwriting [4,5,6]. However, Sb_2Te (or $Sb_{70}Te_{30}$) suffers from poor thermal stability, which is detrimental to the data stability of the memory. Adding specific foreign elements such as Ge, Ag, In and Cr into eutectic SbTe alloys was proved to be an effective way to overcome this obstacle [7,8,9]. Recently, Cr-doped Sb_2Te phase-change recording films were reported by us to exhibit higher thermal stability and reliability than traditional $Ge_2Sb_2Te_5$ for PCM applications [10,11].

Ultrashort operation time is favorable for obtaining a super-high data transfer rate for memory. Our recent studies showed that a gradual crystallization process can be realized by irradiating the same spot of a $Sb_{70}Te_{30}$ phase-change thin film with repeated femtosecond laser (fs-laser) pulses [12,13,14]. However, the ultrafast crystallization process and mechanism of the Cr-doped Sb_2Te film remains poorly understood. Whether the optical-thermal properties of Sb_2Te thin films can be improved by Cr doping in ultrashort-pulse-driven crystallization processes is of great scientific and technical interest.

In this paper, repeated fs-laser pulses induced the crystallization of Cr-doped Sb_2Te films, which was studied in detail with a pump-probe system. The crystallization of films with different Cr contents was compared, and the threshold effects were also comprehensively analyzed.

2. Experiments

Cr-doped Sb_2Te phase-change films were deposited on silicon substrates by direct current magnetron co-sputtering using separate Cr and Sb_2Te targets. The thickness of these films was measured to be about 55 nm by scanning electron microscopy (SEM, Hitachi S-4700). The compositions of these films were measured to be $Sb_{66.4}Te_{33.6}$, $Cr_{8.6}Sb_{58.9}Te_{32.5}$, $Cr_{10.8}Sb_{58.4}Te_{30.8}$ and $Cr_{21.5}Sb_{52.4}Te_{26.2}$ by energy dispersive X-ray spectroscopy (EDS, Oxford INCAEnergy).

As shown in Fig. 1, a pump-probe optical system was assembled to measure the evolution of reflectivity in real time. A mode-locked Ti:sapphire laser with a wavelength of ~800 nm and a pulse duration

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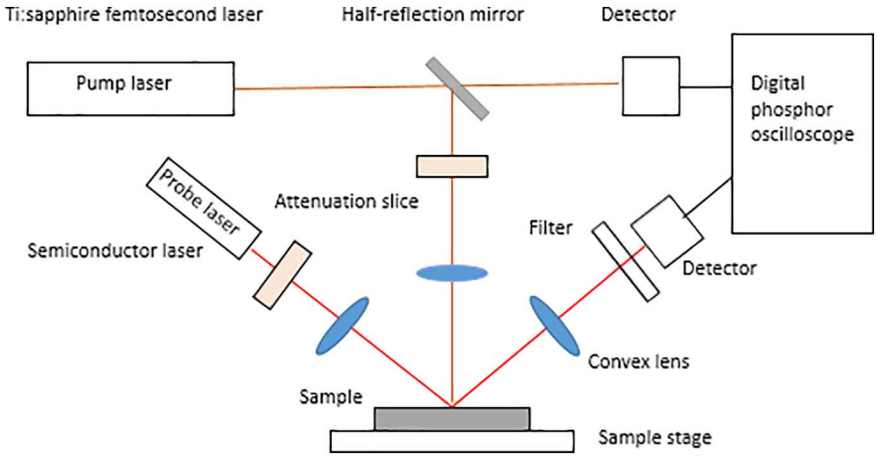

Fig. 1. Schematic of the experimental set up for real-time reflectivity measurements during fs-laser induced crystallization.

of ~130 fs was used as the pumping source. The repetition rate of the pumping laser was 1 kHz. The pump beam was focused on the films with a spot diameter of approximately 1 mm. An electronic shutter was used to control the number of pulses irradiating the films. The probe source was a continuous-wave semiconductor laser (wavelength: ~650 nm). A high-speed silicon avalanche photodiode and a digital phosphor oscilloscope were used to detect and collect the signals, respectively.

A custom-built optical microscope was used to observe the irradiated spots at different fluences. Raman scattering spectra of the films were measured at room temperature by a Horiba LabRAM XploRA confocal microscope. A 532 nm laser was used as the excitation source, and the output intensity was kept low to avoid changing the structure of the films.

3. Results and discussion

Even at a high fluence, completely crystallizing phase-change thin films is difficult using a single fs-laser pulse. However, a high degree of crystallization, which was characterized by a high reflectivity, could be achieved gradually by repetitive laser pulse irradiation of the same amorphous spot [15,16].Real-time reflectivity measurements can allow the indirect observation of the structural evolution process for phase-change materials [17,18]. Fig. 2 shows the fluence-dependent reflectivity contrast (RC) evolution processes of the various as-deposited amorphous Cr-doped Sb_2Te thin films are shown in Fig. 2, which were driven by multiple fs-laser pulses. RC is defined as $\Delta R/R_{am}$, where $\Delta R = R - R_{am}$, R is the measured reflectivity, and R_{am} is the reflectivity of the as-deposited amorphous thin film.

As shown in Fig. 2(a), for the pure Sb_2Te film, when the fluence was 6.9 mJ/cm^2, the RC increased slowly and reached the maximum after about 2500 pulses. As the fluence increased to 12.9 mJ/cm^2, the RC changed more quickly and reached a higher maximum after 2000 pulses. When the fluence increased to 16.1 mJ/cm^2, the RC of the film increased rapidly over 900 pulses and obtained a RC above 100%. However, as we further increased the fluence to 26.3 mJ/cm^2, the RC eventually reached a slightly higher value than those of the lower fluences, but many more pulses (about 2700 and 3000, respectively) were required. A similar trend can also be observed in Fig. 2(b) for the Sb_2Te films with the lowest doping ($Cr_{8.6}Sb_{58.9}Te_{32.5}$). For the $Cr_{10.8}Sb_{58.4}Te_{30.8}$ film, (Fig. 2(c)), with the increase in fluence from 16.1 mJ/cm^2 to 26.3 mJ/cm^2, fewer pulses were required to obtain higher RC values, which is similar to the results in Fig. 2(d) for the highly doped Sb_2Te films ($Cr_{21.5}Sb_{52.4}Te_{26.2}$). Moreover, for the doped Sb_2Te films, the number of pulses (NOP) required to start an obvious RC increase and the NOP to obtain the maximal RC both decreased with the increasing amount of Cr. Some characteristic parameters were extracted

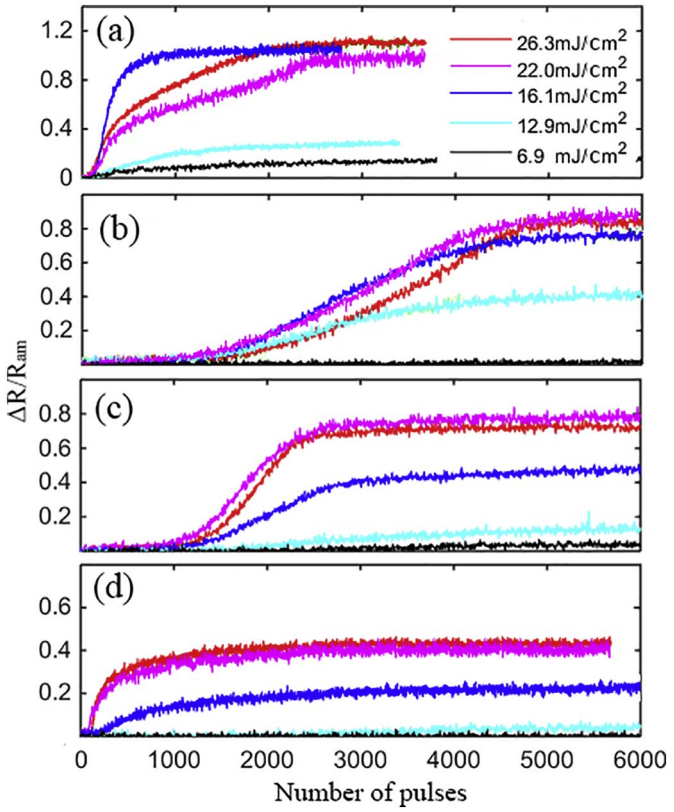

Fig. 2. RC as a function of the number of pulses at different fluences of as-deposited amorphous (a) $Sb_{66.4}Te_{33.6}$ (b) $Cr_{8.6}Sb_{58.9}Te_{32.5}$ (c) $Cr_{10.8}Sb_{58.4}Te_{30.8}$, and (d) $Cr_{21.5}Sb_{52.4}Te_{26.2}$ thin films.

from Fig. 2 and are shown in Table 1. The start and finish of the obvious RC increase corresponded to the start and finish of the gradual crystallization process. The start and finish of the obvious RC increase were defined as 10% and 90% of the maximal RC, respectively.

Note that with a certain NOP, when the fluence increases, the RC will increase at first and then decrease, i.e., there exists an optimal fluence. For example, as shown in Fig. 2(c), the RC reached the maximum of 0.75 with the fluence of 22.0 mJ/cm^2. However, with a higher fluence of 26.3 mJ/cm^2, the final RC decreased to 0.71. The higher the Cr concentration, the higher the optimal fluence is needed for crystallization. The higher required crystallization energy generally indicated better amorphous thermal stability. Moreover, for the Sb_2Te films with lower doping ($Cr_{8.6}Sb_{58.9}Te_{32.5}$ and $Cr_{10.8}Sb_{58.4}Te_{30.8}$), the minimum NOP required for the start of the obvious RC increase is