Laser-induced metastable phase in crystalline phase-change films by confocal Raman spectrometer

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ABSTRACT

Understanding crystallization process in phase-change materials is very important for data storage application. Especially, accurately controlling the metastable phase transition as well as characterizing its structure evolution is still under investigation. In this study, phase transformations have occurs from amorphous to crystalline phases when the phase-change films were irradiated continuously by the 785 nm laser irradiation. By adjusting the laser power, the different metastable phases in conventional $Ge_2Sb_2Te_5$, Sb_2Te_3, ZnSb, ZnSb-Al_2O_3 and ZnSb-ZnO were obtained and distinguished by their different Raman vibration modes. The effect of laser power on the phase-change threshold of these films was studied systematically. Large structural differences induced by laser irradiation were revealed based on the changes in Raman profiles. Our study may offer a new insight into an accurate control of distinct metastable state to realize optical multilevel memory.

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1. Introduction

Phase change memory (PCM) is considered as one of the most promising candidates for next generation memories due to their fast crystallization and amorphization process with order of nanoseconds [1, 2], high data retention for ten years at 85–120 °C [3], good scalability [4], and large cyclability ($>10^{12}$ times) [5]. The conventional PCM has the two-level data storage [6,7], which relies on the rapid and reversible switching of phase-change materials between amorphous phase with high resistance state and crystalline phase with low resistance state upon heating [8]. The capacity of two-level data storage is low, which has become the major obstacle in the maturity of PCM [9]. In contrast, multi-level data storage, which can be achieved by adding another resistance state during phase-change process, has the higher data storage capacity [5]. However, it is currently still a big challenge to characterize multi-level state in the phase-change materials.

It is well known that conventional $Ge_2Sb_2Te_5$ (GST) has an excellent contrast in terms of optical reflectivity and electrical resistivity between amorphous and crystalline states that allows to manipulate the metastable states [10–12]. In the past years, extensive experimental studies on realizing of multilevel states in GST material by thermal annealing have been reported [13–15], where different annealing times were typically applied to crystallize GST film. Additionally, a phase transformation

induced by an electrical excitation accumulation has been observed by *in situ* sheet resistance-temperature measurements due to local Joule heating [16–18]. As an alternative to electrically induced structural changes, the multilevel states can also be driven with short laser pulses irradiation due to high local heating and cooling rates. For example, structural change of GST film was investigated by femtosecond (fs) and nanosecond (ns) single laser pulses ($\lambda = 248$ nm) with pulse durations of 500 fs and 20 ns, respectively, were applied in the crystallization experiments in order to generate the metastable phase [19,20]. The spot size of the ns rectangularly shaped laser beam was about 24×6 mm^2 with almost a top hat intensity distribution, while the fs laser beam spot size was about 2×3 mm^2 [20]. However, the detailed structural information is still lacking since it is very hard to detect structure by power X-ray diffraction (XRD) and Raman spectra for such thin films with small laser crystallized areas of 100×59 μm^2.

Laser-induced phase transformations of GeS_2-Sb_2S_3 chalcogenide glasses were studied by a laser confocal Raman spectrometer using an Ar ion laser with a wavelength of 488 nm, as reported by C.G. Lin, et al. [21]. Structure and optical properties of Raman laser-induced phase change in Ge-Sb-Se films were also investigated in our previous work [22], resulting in the determination of the threshold power for crystallization and amorphization. The amorphous, metastable and stable phases for the annealed Si-Sb-Te films can be distinguished visually by the change in the surface morphology during Raman scattering experiments [23]. These investigations indicate that Micro-Raman spectroscopy is a powerful tool to observe laser-induced crystalline phases. However, these *ex-situ* observations in thermal-annealed or laser-irradiated films fail to directly present *in situ* information regarding

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the metastable phase during phase transformation from amorphous to crystalline state. Therefore, the real-time structural change in the films during phase-change process is unclear.

In this paper, we demonstrated that, the real-time structural change from amorphous to crystalline state (metastable phase, stable phase or mixture of both) induced by laser irradiation can be recorded clearly in phase-change films, such as GST, Sb_2Te_3, ZnSb, ZnSb-Al_2O_3 and ZnSb-ZnO. By analyzing the evolution of Micro-Raman spectra, the Raman vibrational mode in the metastable phase can be clearly observed to confirm the phase transition, yielding threshold information of their phase transformation behavior. Furthermore, the main Raman peaks shift as functions of laser irradiation power have been discussed in detail.

2. Experimental

$Ge_2Sb_2Te_5$, Sb_2Te_3 and ZnSb thin films with a thickness of ~120 nm were deposited on Si and thermally oxidized Si wafers at room temperature by the magnetron sputtering method, respectively. Nano-composite ZnSb-Al_2O_3 and ZnSb-ZnO films with the same thickness were also deposited by magnetron co-sputtering method using individual ZnSb and Al_2O_3/ZnO targets, respectively. In each run of the experiment, the base and working pressures were set to be 4.6×10^{-4} and 0.2 Pa, respectively. The Ar gas flow was set to 47.6 mL/min. The direct current power (P_{dc}) was fixed at 30 W and applied to a ZnSb target of 50 mm diameter. The amount of Al_2O_3/ZnO in the ZnSb films was adjusted by varying the radio frequency power (P_{rf}) applied to the Al_2O_3/ZnO target of 50 mm diameter. The P_{rf} was fixed at 1, 5, and 10 W for Al_2O_3, 3, 8 and 21 W for ZnO, respectively, in order to vary the oxide-doping concentration. All the samples were prepared and measured in vacuum for avoiding the surface oxidation. The composition of the films was determined by energy dispersive spectroscopy (EDS). The thickness of the film was measured by surface profiler (Veeco Dektak 150). Continuous 785 nm laser irradiation was performed on a laser confocal optical microscope stage with a 50× magnification objective (NA = 0.75) equipped in a Renishaw InVia Raman spectrometer. The frequency resolution is ±0.1 cm^{-1}. The surface morphology of irradiated films was observed by optical microscope and its Raman spectrum was real-time recorded by the same laser with an excitation power from 0.25 to 500 mW for 5 s in order to distinguish the different bonds' vibrations in the metastable phases for the investigated films.

3. Results and Discussion

3.1. Raman Spectra of $Ge_2Sb_2Te_5$ Film

Fig. 1(a) displays the Raman spectra of $Ge_2Sb_2Te_5$ (GST) film irradiated at the different laser power from 0.25 to 500 mW, where the real-time structural change in the laser-irradiated GST film is evident with increasing laser power. For the film irradiated at 0.25 mW for 5 s, there is a broad band ranging from 100 to 175 cm^{-1}. Two broad peaks, located at ~125 cm^{-1} (peak A) and ~150 cm^{-1} (peak B), overlap with each other in this region. This is well agreement with the previous reports on amorphous GST [24, 25], implying that the film irradiated at a low laser power exhibits an amorphous (AM) nature. The two peaks A and B are A_1 mode in $GeTe_{4-n}Ge_n$ (n = 0,1,2) tetrahedra [24] and Sb—Te bonds' vibrations in the Sb—Te_3 units [25], respectively. In addition, a weak and broad Raman band located at ~220 cm^{-1} (peak C) is assigned to the F_2 mode of $GeTe_4$ tetrahedra [26]. In the low-frequency region of the spectra, a peak at ~56 cm^{-1} (peak D) can be observed, which is related to the E mode of $GeTe_4$ tetrahedra [26]. It is found that, the broaden feature of the Raman spectrum can be kept at a laser power ranging from 0.25 to 5 mW. With further increasing laser power, the peaks A and B gradually shift towards lower and higher wavenumber as shown in Fig. 1(b), respectively. The gradual separation of the two peaks during laser-induced crystallization process becomes
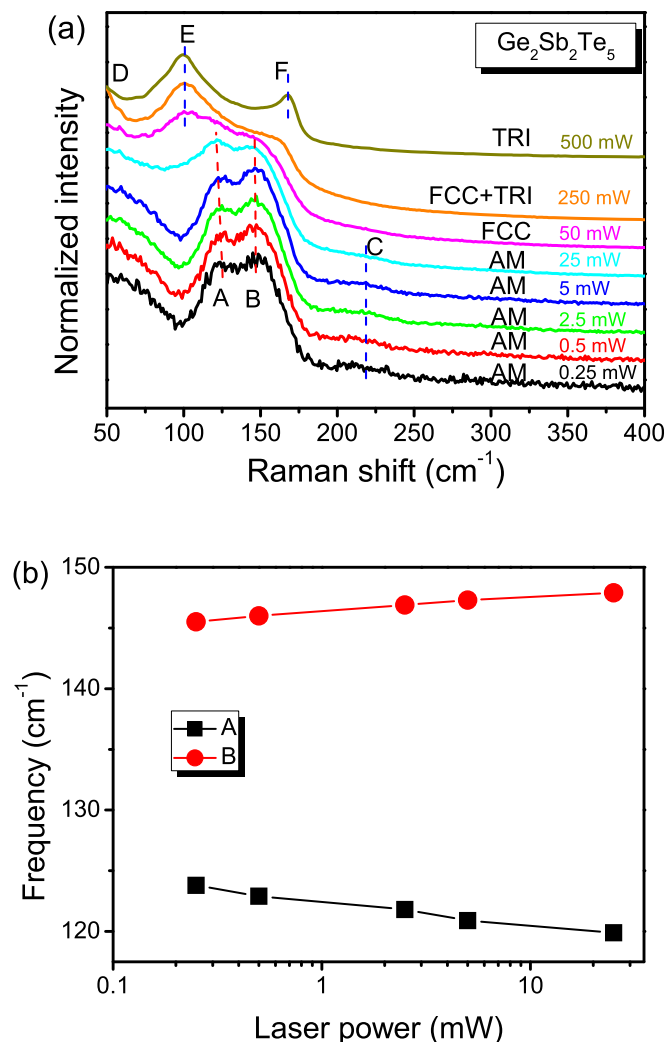

Fig. 1. (a) Raman scattering spectra of $Ge_2Sb_2Te_5$ by laser irradiation with different power for 5 s; (b) The frequency variation of the two main Raman peaks (A, B) in AM state as functions of laser power.

severer. The reason is that laser irradiation induces the bond recombination among Ge, Sb, Te atoms. Higher laser power of 25 mW is easier to break chemical bonds, such as Ge—Te and Sb—Te, et al., resulting in a regular shift in Raman peaks. When the laser power reaches 50 mW, the peak A is converted into peak E because the provided energy is enough large to cause the phase transition from AM to face-centered cubic (FCC) phase. The new peak E located at ~105 cm^{-1} is related to the A_1 mode of $GeTe_4$ corner-sharing tetrahedra [27]. Note that the peak E can be observed in the FCC state, which is in well accordance with previous studies on the thermal-annealed GST [28,29]. The results reveal that the GeTe component of GST alloys is mainly responsible for the phase transition from AM to FCC state. Such transition can be correlated to the unique adjustments of atomic and electronic configurations surrounding the central Ge atoms [30], namely the tetrahedrally (covalent [31], sp^3) bonded structure in AM phase and the octahedrally (resonant [32,33], p—p) bonded structure in the FCC phase, respectively.

On the other hand, the peak B located at 150 cm^{-1} gradually shifts towards high wavenumber and disappears until 250 mW. It can be found that the intermediate states appear in the 250 mW-irradiated film. Instead, a new sharp peak F at ~172 cm^{-1} appears in the GST film irradiated at 500 mW, which confirms the basic formation of the stable trigonal (TRI) phase. Not surprisingly, 20% of the Ge sites in the FCC crystals are vacant, and the Ge/Sb/vacancies randomly occupy one sublattice [34]. These vacancies are theoretically predicted to be