Picoseconds Laser-Induced Reversible Phase Change of Cu-Sb₂Te Thin Films

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Abstract. Cu-doped Sb_2Te is extensively used for phase change optical storage. The phase change dynamics in Cu-doped Sb_2Te thin films by Picoseconds laser pulses were studied. The crystallization threshold and the reflectivity contrast of the Cu-Sb_2Te alloy increased with the Cu content, the reflectivity contrast of about 28% was obtained on Cu-doped Sb_2Te film with the Cu content of 27at.%, and the reversible phase change realized due to the ps laser pulses irradiation in strong-weak cycles.

1. Introduction

Since the threshold switching was demonstrated by Ovshinsky [1], Phase change optical recording has been an attractive and mature technology. The promising features, such as the compact storage format, noncontact recording process, and long-term stability, triggered intensive research to further improve the performance of optical discs. Crystallization process corresponds to an erasing or a set operation in phase change optical storage. Short crystallization time will be favorable for obtaining high data transfer rate, and the stability of amorphous state is in favor of data non-volatility. So searching the materials with short crystallization time and higher crystallization threshold is very important. Many phase-change materials have been investigated extensively in last several decades [2-9], relying on their attractive application on reversible phase-change optical discs and nonvolatile storage memory such as GeSbTe, AgInSbTe.

The mostly commonly phase change materials are based on the Ge-Sb-Te or Sb-Te materials system, and doping are often applied to modify the switching properties such as switching speed and thermal stability. Jiang et al [10] investigated theoretically the crystallization kinetics of the films, to which small amount of foreign elements such as Cu, Co, Ag and Sb was added. Chen et al [11] investigated the crystallization temperature of the Ag and Cu doped Sb_2Te_3 amorphous film. The investigation indicated doping Ag and Cu can improve room temperature stability of Sb_2Te_3 amorphous film due to the increased crystallization temperature. Lankhorst [12] suggested a model for the calculation of the glass transition temperature Tg of phase change materials as a function of material composition. Recently Cu-doped Sb_2Te is extensively used for high speed phase change random access memory (PCRAM) [13]. And the thermal stability and crystal structure of the composition Cu-Sb_2Te were studied [14]. However, the investigation of crystallization induced by ps laser pulse on Cu-Sb_2Te alloy thin films has not reported.

In this paper, we investigated the crystallization process of Cu-Sb$_2$Te alloy film with variable Cu concentration triggered by ps laser pulse. The crystallization threshold and the reflectivity contrast increased with the Cu concentration. The reflectivity contrast of about 28% was obtained on Cu-doped Sb$_2$Te film with the Cu concentration of 27at.%, and the reversible phase change realized due to the ps laser pulses irradiation in strong-weak cycles.

2. Experiment

200-nm-thick Cu-Sb$_2$Te films were deposited on SiO$_2$/Si (100) substrates by magnetron co-sputtering using separate Cu, Sb, and Te targets of 50mm in diameter. The film composition could be controlled by the change in the sputtering power applied to the targets. The concentration ratio of Sb to Te was fixed to 2:1, and Cu concentration was changed from 2at. % to 27at. %.

A real-time reflectivity measurement was setup. Light source for pumping was a picosecond (ps) mode-locked Neodymium Yttrium Aluminum Garnet (Nd:YAG) laser with a pulse duration of 28 ps and wavelength of 532 nm (EKSPLA PL2143B). The pulse energy stability is better than 5% at 532 nm. The laser beam was focused by a convex lens on the surface of sample with a spot diameter of about 2mm. CW probe light beam with wavelength of 633 nm from a He–Ne laser (Melles Griot) was incident at an angle of 15^0 and focused on the center of irradiated spot with a spot diameter of about 0.2mm. The reflected probe beam was detected by a high-speed silicon avalanche photodiode (rise time: 220 ps) and a 500MHz digital phosphor oscilloscope (Tektronix 5052B) with a total time resolution of 2 ns. Raman spectra of the irradiated areas on Cu-Sb$_2$Te thin film were measured on the conditions of NA 0.4 and excitation laser wavelength 514nm by Micro-area Raman microscope (Renishaw).

3. Result and Discussion

As the potential phase change material, the optical property of the Cu-Sb$_2$Te alloy thin film was a problem worth studying. Simone Raoux [13] calculated the glass transition temperature (Tg) with the model suggested by Lankhorst [14].

$$T_g = 3.44H_{tot} - 480$$

$$H_{tot} = \sum_{A,B} n_{AB}H_{AB}$$

$$H_{AB} = \frac{(H_{AA} + H_{BB})}{2} + 96.14(S_A + S_B)^2$$

Where H$_{tot}$ (in kJ/mol) is the total enthalpy, n$_{AB}$ presents the number of bands between element A and B, H$_{AB}$ presents hetero-nuclear band enthalpy, H$_{AA}$ and H$_{BB}$ are homo-nuclear enthalpy, S$_A$ and S$_B$ presents the electro-negativities of the elements A and B. The calculation shows an increase in glass transition temperature with higher doping until the ratio of Cu: Te reaches the value 2:3.

The ultrafast phase change induced by Picoseconds laser irradiation due to an ultrafast heating. Then we studied the phase change process induced by Picoseconds laser irradiation. The curves in Fig.1 were absolute values of the reflected probe light because of using DC coupling of phosphor oscilloscope. So the reflected probe light intensity before trigging (the part of curve in front of zero point) was equal to the reflectivity of the stable state induced by the last time irradiation. The interval of two adjacent irradiations was about 1-2 minutes, which was enough to reach a stable state of the structural relaxation or crystallization process on the thin film induced by the irradiation last time. As shown in Fig.1 (a), the crystallization process on Cu-Sb$_2$Te alloy film presented gradual increasing characteristic due to the weaker laser irradiation. After the forth irradiation, the reflected probe light intensity did not increase, and the curve presented a straight line and coincided with stable reflected probe light intensity (the part after 100ns) induced by the third irradiation. This phenomenon indicated that the fully crystallization completed due to three irradiations. If the pump pulse was stronger, the reflected probe light intensity did not increase after the second irradiation as shown in Fig.1 (b). The fully crystallization obtained by one irradiation with the pulse fluence of 33.2mJ/cm^2. So the threshold

of the fully crystallization was 33.2mJ/cm^2 and that of Cu-Sb$_2$Te alloy film with variable Cu content could be conformed in this way.
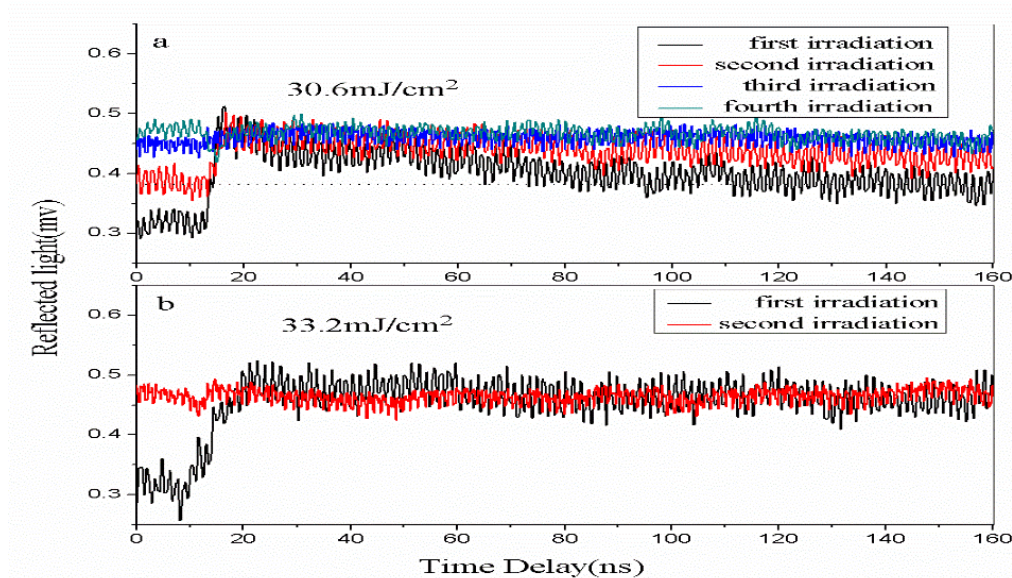
Figure 1. The evolutions of the reflected probe light intensity (represented normalized reflectivity) induced by multiple irradiation by picosecond laser pulses with invariable fluence on the same spot on the Cu-Sb$_2$Te alloy thin film with the Cu concentration of 27 at. %. The fluence of the laser pulses were (a) 30.6mJ/cm^2 and (b) 33.2mJ/cm^2 respectively.
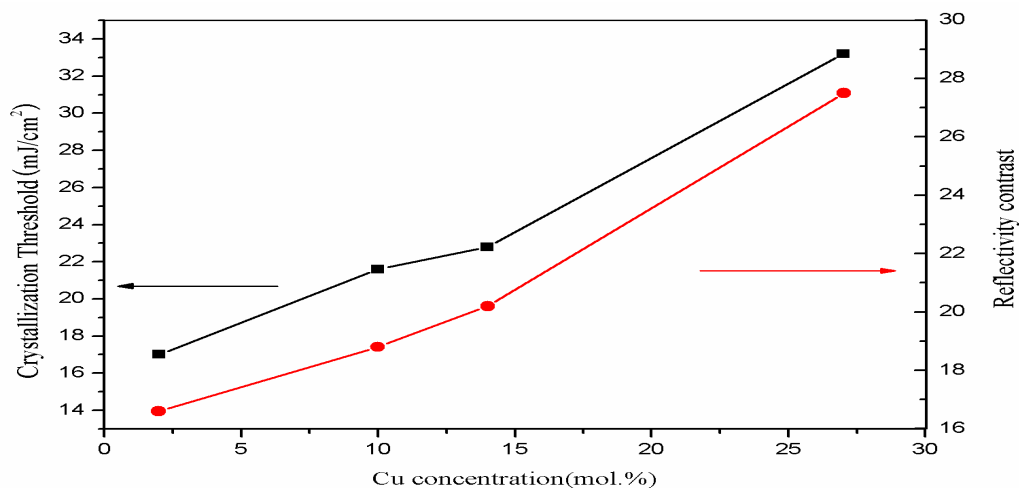

Figure 2. The evolutions of the crystallization threshold (square black line) and the reflectivity contrast (dot red line) along with Cu concentration in the Cu-Sb$_2$Te film.

The experimental crystallization threshold (square black line) and the reflectivity contrast (dot red line) increased with the Cu content, as shown inFig.2. The reason of increasing of the crystallization threshold was that the doped Cu altered the bonds structure of Sb$_2$Te. The addition of Cu into Sb$_2$Te may lead to the formation of covalent bonds with ionic tendency since the electro negativity of Cu (1.9) is lower than those of Sb (2.05) and Te (2.1). Consequently, the bonding force may enhance and the atoms become less mobile. There are several mechanisms such as bond breaking and bond-angle deviation in crystallization process. The atomic rearrangement requires much more energy to overcome the rigid atoms network due to the complex branching and cross links [15].

The high crystallization threshold means the excellent thermal stability or data retention of phase change memory in high temperature application. The crystallization threshold fluence of the single-layer Sb-rich AgInSbTe films [16] upon irradiation with 120fs laser pulse is 21.76mJ/cm^2. The crystallization threshold fluence of the $Ge_2Sb_2Te_5$ films [9] upon irradiation with picosecond laser pulse is 24mJ/cm^2. The crystallization temperature increased from 225°C to 250°C when13at. % nitrogen was added into the $Si_{10.5}Sb_{89.5}$ film [17] Compared to the crystallization temperature of GST. In contrast, the Cu-Sb_2Te alloy thin film has higher crystallization threshold, so it has more excellent data retention.

In addition, the high reflectivity contrast$R_c = 2 * (R - R_0)/(R + R_0) * 100\%$between crystalline and amorphous phase means the preferable data veracity. The reflectivity contrast of Cu-Sb_2Te alloy thin film reached 16.2, 18.6, 20.3, and 23.4 with varying Cu content respectively. The reason of increasing of the reflectivity contrast was that the varying concentration of doped Cu altered differently the optical constant of crystalline thin film, and the alteration of amorphous state was minor due to the absence of long-range order. The reflectivity contrast of 37% was obtained by doping Cu and Ag into Sb_2Te_3 which was reported in the investigation by Y.M. Chen et al [11].
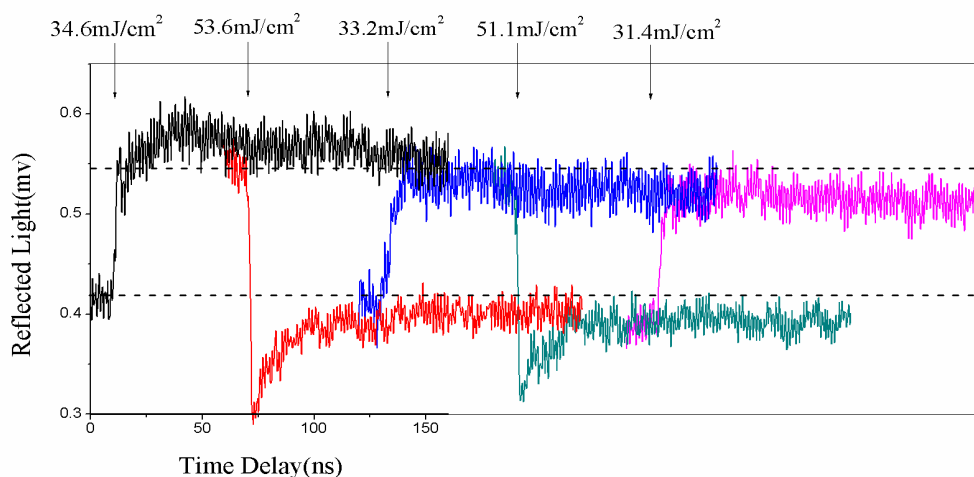
Figure 3. The reversible phase change in Cu-Sb2Te film with the Cu concentration of 27at. % induced by ps-pulse with strong-weak cycles. The curves were horizontally shifted to improve the visibility.

Crystallization occurred when the fluence of the pulse reached the crystallization threshold. On the other hand, the irradiation spot on the Cu-Sb_2Te film melted when the fluence of the pulse exceeded the melting threshold and then quickly cooled, as a result, amorphous point was obtained. As shown in Fig.3, reversible phase change realized due to the ps laser pulses irradiation in strong-weak cycles.

For reversible phase change optical storage, the recording process is achieved by an intense and short laser pulse, which melts the spot on thin film that then is converted into the amorphous state on quenching. The erasing process is often achieved by a moderate and long pulse, which heats the material to a temperature slightly above the crystalline temperature. As shown in Fig.3, the Cu-Sb_2Te alloy thin film is a potential rewritable phase change optical storage material. Meanwhile, the reflectivity contrast ceaselessly reduced each round due to the ablation and peeling occurred from every melt on the film surface. But for the practical optical memory storage device, the ablation and peeling will not occur because the si/sio$_2$ protect-layer on the sample is necessary.

4. Summary
The Cu-Sb_2Te component thin films were investigated for high speed phase change optical recording. The phase change of the Cu-Sb_2Te film was studied in this paper. The crystallization threshold and the reflectivity contrast increased with the Cu content, because the different content of doped Cu altered differently the bonds structure and the optical constant of the alloy thin film. The reversible phase

change realized due to the ps laser pulses irradiation in strong-weak cycles. In summary, the Cu-Sb$_2$Te alloy thin film was a potential phase change material.

5. Acknowledgments

6. References

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