Laser induced crystallization of as-deposited amorphous $Ge_2Sb_2Te_5$ films

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Crystallization is induced by pulsed laser irradiation of as-deposited amorphous $Ge_2Sb_2Te_5$ films. Changes of the irradiated areas have been analyzed with the reflectivity contrast. As laser fluences increasing, the reflectivity contrast increases from 0% − 2% to 14% − 16%, which indicates the structure of as-deposited films transforms from amorphous to crystalline phases. The process of crystallization driven by the movement and rearrangement of atoms is described. And also the influence of the pulse duration on the threshold of crystallization is discussed, the results show that a lower threshold of crystallization can be produced for as-deposited films irradiated by the laser with short pulse duration. However, by the laser with long pulse duration, crystallization can only be formed with a higher threshold. The crystallization of films by irradiation of laser pulses is studied by Raman spectra.

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The problem of laser-induced crystallizations in amorphous films has been the scope of intensive experimental and theoretical studies currently. Of particular interest is the process and the mechanism of crystallization induced by pulsed laser. Those processes are accompanied by the modification of the free energy of the system and normally by changes in the physical properties which have been intensively studied in the case of amorphous semiconductors. Laser-induced structural relaxation and phase transition in materials such as Ge[1], Si[2,3], GeSb[4], and GaAs[5] have been investigated extensively and a series of interested results have been obtained. In order to understand the further detail information, we study crystallization of amorphous $Ge_2Sb_2Te_5$films induced by three pulsed lasers with different powers.

$Ge_2Sb_2Te_5$ films can realize the reversible transformation of small areas between the amorphous and crystalline phases using a single beam pulsed laser. The amorphous and crystalline phases have different optical properties, therefore the films have been applied to the rewritable optical data storage widely in the past several years [6,7] and will also be one of the promising semiconductor materials for optical memory switch in the future.

As an important optical data storage media, the crystallization behavior of $Ge_2Sb_2Te_5$ films has been analyzed on various time scales in order to determine the crystallization mechanism[8]. In this paper, we find laser fluences play an important role in crystallization of as-deposited amorphous films. At certain pulse duration, different laser fluences have the different effect on crystallization. By measuring the reflectivity contrast of as-deposited amorphous $Ge_2Sb_2Te_5$ films before and after irradiation, we present the process and the mechanism of crystallization in as-deposited amorphous $Ge_2Sb_2Te_5$ films induced by different laser fluences and also expatiate the influence of different laser pulses on the threshold of crystallization.

As-deposited amorphous $Ge_2Sb_2Te_5$ films with a thickness of 50 nm were deposited on the K9 glass by dc-magnetron sputtering using a stoichiometris target with a diameter of 180 mm. The target is bonded to a water cooled copper plate. The base pressure in the deposition chamber is typically 1.8×10^{-3} Pa. Sputtering is performed using Ar ions at a pressure of 6×10^{-1} Pa.

An argon laser at 514.5 nm, was used to irradiate as-deposited amorphous $Ge_2Sb_2Te_5$ films and monitor the reflectivity contrast upon the irradiated areas as shown in Fig. 1. The pulsed laser with 22.5 mW and pulse duration as short as 50 ns was employed. It is focused onto the film by a microscope objective with a number aperture (NA) of 0.85, and the laser spot diameter was about 1 μm. A low power probe pulse was used to measure the reflectivity before and after irradiation. This process was illustrated as following, the first laser pulse is at low power and is used to determine the reflectivity of a local region of as-deposited $Ge_2Sb_2Te_5$ films. The second laser pulse is a higher power and locally heats the amorphous films to a temperature sufficient for the structure transition of the crystalline phase. The third pulse is again used to determine the reflectivity. After each area irradiating by pulsed laser, films were moved to a fresh area. The reflectivity contrast ΔR was used to describe crystallization which is expressed as

$$\Delta R = 100\% \times 2 \times (R_\mathrm{f} - R_\mathrm{i})/(R_\mathrm{f} + R_\mathrm{i}),$$

where R_i and R_f are the reflectivity before and after irradiation of laser pulses, respectively.

The spectra were measured using micro-Raman methods; the results presented here were obtained using a JOBIN YVON(T6400) Raman microscope with a 100×/0.8-NA objective and excitation at 514 nm. The intensity of the excitation was adjusted to a level which produced no discernible change in the spectrum of the specimen. All Raman experiments were carried out in air at room temperature.

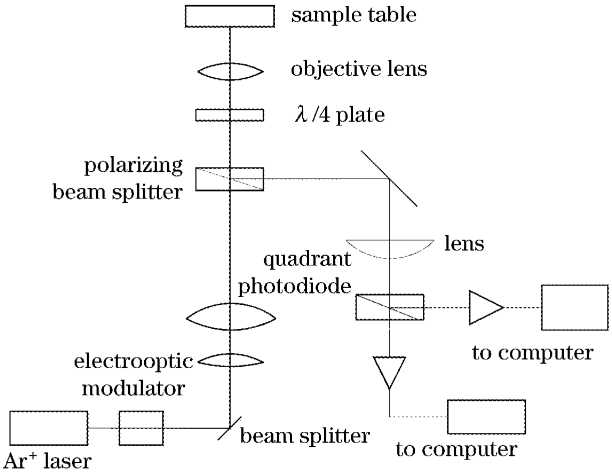

Fig. 1. Schematic of experimental setup of pulsed laser irradiation. The laser pulses source operates at 514.5 nm and produces pulsed laser power up to 22.5 mW and pulse duration as short as 50 ns.

As shown in Fig. 2, the reflectivity contrast of as-deposited amorphous $Ge_2Sb_2Te_5$ films with 60-ns laser pulses irradiation increases from 0% – 2% to 14% – 16% when laser fluences change from 8.6 to 172 mJ/cm^2. For laser fluence lower than 50 mJ/cm^2 there is no appreciable change in the reflectivity contrast. So this laser fluence is referred to hereafter as the crystallization threshold that corresponds to the onset of the crystallization. For laser fluences higher than 50 mJ/cm^2, the reflectivity contrast begins to transform and has an absurdly increment. For laser fluences in the 50 – 130 mJ/cm^2 range, the observed reflectivity contrast upon irradiation of different laser fluences increases from 2% to 15%. Laser fluences higher than 130 mJ/cm^2 lead to keep about 15% in the reflectivity contrast. This laser fluence is defined as the ablation threshold that corresponds to the end of crystallizaiton and the beginning of the ablation of films irradiated by high laser fluence. Reflectivity before and after irradiation upon 60-ns laser pulses with various fluences is shown in Table 1. The reflectivity of films after irradiation of laser pulses is higher than that of as-deposited films, which is related to the crystallization of film upon irradiation of laser pulses. For Fig. 3, as-deposited amorphous $Ge_2Sb_2Te_5$ films are irradiated by 100-ns laser pulses. The observed reflectivity contrast is similar to those upon irradiation of 60-ns laser pulses. However, for 100-ns laser pulses, thresholds of the crystallization and the ablation are 100 and 225 mJ/cm^2, respectively. Two of them are higher than those irradiated by 60-ns laser pulses. For laser fluences lower than 100 mJ/cm^2, in Fig. 3, the reflectivity contrast is less than 2%. When the laser fluence is in the 100 – 225 mJ/cm^2 range, the reflectivity contrast changes distinctly from 2% to 14% with the increasing of laser fluences. As laser fluences further increase, the ablation of films ocurrs. Reflectivity before and after irradiation by 100-ns laser pulses with various fluences is shown in Table 2.

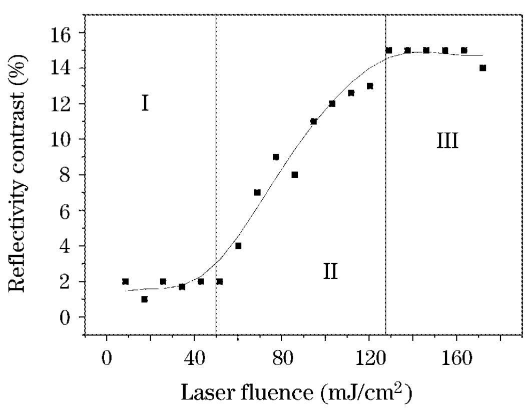

Fig. 2. Relationship between reflectivity contrast and laser fluence (pulse duration: 60 ns; the curve shown is a guide to the eye).

The reflectivity contrast by irradiation of 300-ns laser pulses is shown in Fig. 4. Here, we can observe that the reflectivity contrast of as-deposited amorphous $Ge_2Sb_2Te_5$ films has the similar change to that of 60- and 100-ns laser pulses. But thresholds of the crystallization and the ablation are 300 and 688 mJ/cm^2, respectively, and higher than those irradiated by 60- and 100-ns laser pulses. When laser fluences are lower than the crystallization threshold, the reflectivity contrast is also less than 2%. However, laser fluences in the 300 – 688 mJ/cm^2 range cause to increase from about 2% to 15% in the reflectivity contrast. After laser fluences higher than 688 mJ/cm^2, films are ablated. Reflectivity before and after irradiation upon 300-ns laser pulses with various fluences is shown in Table 3.

For different pulse durations, 60, 100, and 300 ns, the reflectivity contrasts have the same trend when laser fluences change. The change of the reflectivity contrast indicates that crystallization is induced by pulsed laser. As shown in figures, laser fluences can be divided into three zones considering changes of the reflectivity contrast. In the first zone (I), the reflectivity contrast is about 0% – 2%, which indicates that laser fluence is too insufficient to lead to the movement and rearrangement of atoms and to cause crystallization in as-deposited amorphous films. Enhancing the laser fluence, the reflectivity contrast

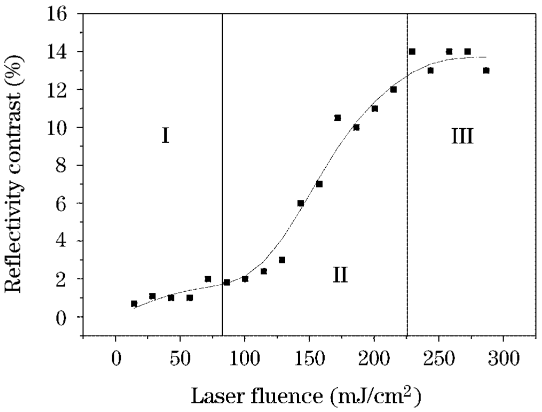

Fig. 3. Relationship between reflectivity contrast and laser fluence (pulse duration: 100 ns; the curve shown is a guide to the eye).

Table 1. Reflectivity before and after Irradiation by 60-ns Laser Pulses with Various Fluences

Fluence (mJ/cm^2)	25.80	51.59	103.18	120.38	128.98	146.18
Reflectivity before Irradiation (a.u.)	73	74	76	77	77	77
Reflectivity after Irradiation (a.u.)	75	76	86	88	90	90

Table 2. Reflectivity before and after Irradiation by 100-ns Laser Pulses with Various Fluences

Fluence (mJ/cm^2)	42.99	100.32	128.98	186.31	229.30	243.63
Reflectivity before Irradiation (a.u.)	74	75	76	75	73	75
Reflectivity after Irradiation (a.u.)	75	77	79	83	84	85

Table 3. Reflectivity before and after Irradiation by 300-ns Laser Pulses with Various Fluences

Fluence (mJ/cm^2)	128.98	300.96	386.94	558.91	687.90	773.89
Reflectivity before Irradiation (a.u.)	65	59	54	54	56	58
Reflectivity after Irradiation (a.u.)	66	60	57	65	65	67

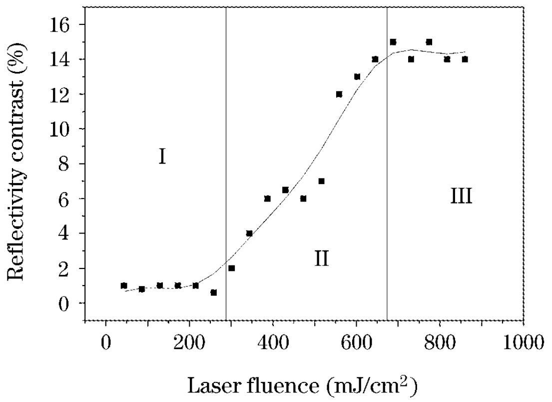

Fig. 4. Relationship between reflectivity contrast and laser fluence (pulse duration: 300 ns; the curve shown is a guide to the eye).

increases from 2% to about 14% – 16%. In the second zone (II), as-deposited amorphous $Ge_2Sb_2Te_5$ films absorb more energy than that of the first zone, driven by higher energy, the ability to atomic mobility is increased, and atoms could obtain more energy and overcome the barrier to rearrange, then some small crystalline nuclei are formed in the local as-deposited amorphous area. After nucleation, small nuclei have still sufficient energy to grow, therefore big crystalline nuclei will be formed in both films irradiated by 60-ns laser pulses and that irradiated by 100-, 300-ns laser pulses. The crystallized areas become large gradually; finally the whole area upon irradiation of pulsed laser is crystallized, which leads to the different reflectivity of as-deposited films before and after laser irradiation. As a result, the reflectivity contrast occurs to change. Laser fluences higher than the ablation threshold will cause the ablation of films, as shown in the third zone (III).

A comparison between crystallization processes that takes place when irradiating with 60, 100, and 300 ns proves that the crystallization and ablation threshold depend on the pulse duration. The laser with short pulse duration can initiate and complete crystallization for as-deposited amorphous $Ge_2Sb_2Te_5$ films at the lower threshold whereas long pulse duration requires the higher threshold for finishing the transformation of as-deposited amorphous $Ge_2Sb_2Te_5$ films. The reason that the crystallization and the ablation threshold by irradiation of 60 ns are smaller than those by irradiation of 100 and 300 ns might be related to pulse duration. For the laser with long pulse duration, the amount of the thermal diffusion transferring to the glass substrate increase with the increasing of the irradiating time, while the laser pulse is still being absorbed by the as-deposited film[9]. The irradiating time of the short pulse duration is shorter than that of the long pulse duration, the thermal diffusion of the short pulse duration is less, moreover, the laser with a short pulse duration, such as 60 ns, has the higher peak temperatures and less thermal diffuse, so a lower laser fluence could lead to crystallization and ablation of films. However, for the long pulse duration, for example 100 and 300 ns, there is a lower peak temperature and a distinct thermal diffuse effect, so the occurrence

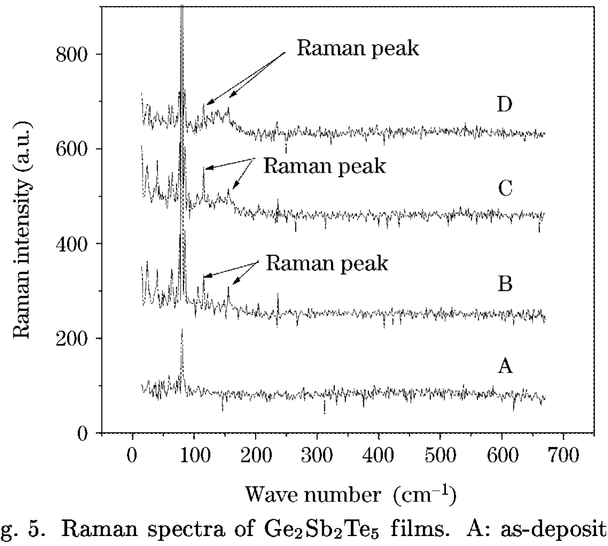

Fig. 5. Raman spectra of $Ge_2Sb_2Te_5$ films. A: as-deposited films; B: crystallized films by irradiation of 60-ns laser pulses at low energy; C: crystallized films by irradiation of 60-ns laser pulses at middle energy; D: crystallized films by irradiation of 60-ns laser pulses at high fulence.

of crystallization requires a high laser fluence comparing with the laser with short pulse duration.

Figure 5 is the Raman spectra of $Ge_2Sb_2Te_5$ films. The Raman spectra of the as-deposited films show no peak, which confirm the amorphous nature. B, C, and D in Fig. 5 are the Raman spectra of films by irradiation of 60-ns laser pulses with various fluences. The fluecne for B is about the crystallization threshold, for D is about the ablation threshold, and for C is between the above two thresholds. The distinguish Raman peak between 100 and 150 cm^{-1} indicates that films have been crystallized after irradiation of 60-ns laser pulses. The position of Raman peak is identical to experimental results made by Tominaga[10]. Increasing of the intensity of Raman peak from B to D proves an increase in the extent of crystallization with fluences increasing. The Raman spectra of films upon irradiation of 100-, 300-ns laser pulses with various fluences are similar to those by irradiation of 100-ns laser pulses (the spectra are not shown).

In summary, the laser fluence and pulse duration have the influence on the crystallization of amorphous $Ge_2Sb_2Te_5$ films. At certain pulse duration, crystallization before and after irradiation is related to the laser fluence. For laser fluence higher than the crystallization threshold, the extent of crystallization increases with the increasing of laser fluence. For the laser with 60-, 100-, and 300-ns pulse durations, different thresholds of crystallization can be produced in amorphous $Ge_2Sb_2Te_5$ films. The Raman spectra confirm the crystallization of films by irradiation of laser pulses.

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