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Microscopy study of laser-induced phase change in Al–Cu film

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Microscopy studies of the structural changes of the vapour-quenched $Al_{71}Cu_{29}$ films induced by laser irradiation are presented along with the discussion of the phase change mechanism. This leads to a high interest in a fast phase-change phenomenon between the amorphous and metastable crystalline states.

1. Introduction

The study of materials phase transition under pulse laser irradiation is of interest in phase-change optical recording. Over the last few years, materials of some semiconductor compounds such as GeTe [1], $GeSb_2Te_4$ [2], In_3SbTe_2 [3] have been highlighted because they possess fast phase-change speed. However, some low-melting metallic alloys may also be potential candidates owing to some of their unique crystallization properties. For example, a fast phase transition between amorphous and metastable crystalline states has frequently been observed in some aluminium- and copper-based alloys under certain circumstances [4–6]. This phenomenon has also been observed in our previous study on the evaporated Al–Cu film. That is, the first crystallized structure of the vapour-quenched amorphous phase tends to be an fcc single phase (or supersaturated solid solution), and on annealing, it undergoes a step-by-step phase transformation process (through metastable states) before reaching the final equilibrium state [7]. Interest continues in the laser-induced phase change behaviour in these materials. With this purpose, we present here a study of the phase transition of $Al_{71}Cu_{29}$ alloy film under various pulse laser irradiations, with particular interest in the kinetics between the pulse laser and the materials interaction.

2. Experimental procedure

$Al_{71}Cu_{29}$ alloy films were produced by co-deposition of two components (pure aluminium and copper at a pressure of 5×10^{-5} torr (1 torr = 133.322 Pa). Both cooled (by liquid-nitrogen) and uncooled (room temperature) sapphire substrates were used so that both amorphous and crystalline phases could be formed, respectively (the structure was subsequently determined by the electron diffraction analysis). The typical deposition rate was controlled at about 0.8–1.2 nm s^{-1}, and the final thickness of the film was in the range 40–60 nm. Film composition was then determined by an EDAX energy dispersive spectrometer. The substrates were pre-coated with collodion films (about 30 nm thick) because it permits easy removal of the deposits on to TEM grids. Laser irradiation was then carried out on these substrate-free films on the TEM grids, which were convenient for subsequent structural study by TEM (Jeol 2000 EX). The irradiation was performed in a static optical recording test system which was specially designed, using a He–Ne laser ($\lambda = 632.8$ nm) with adjustable power (up to 18 mW) and pulse duration (100 ns–40 μs). The focused laser beam was about 1 μm (HWMP) diameter.

3. Results and discussion

3.1. Structure and morphology of irradiated spots

The first set of laser irradiations was carried out on the sample transformed from the uncooled substrate in which the initial state is an fcc single phase. The laser power used was fixed at 17 mW but the pulse duration varied. Fig. 1 shows a series of TEM morphologies and electron diffraction patterns of the irradiated spots obtained with the various laser pulses. Change in morphology and structure can be seen. In Fig. 1a, a small faint mark can only just be distinguished, indicating the 100 ns pulse is just below the threshold of mark-making. An increase in the pulse duration to 200 ns results in the formation of an amorphous spot, plus a damage hole in the centre. The high-resolution images of the structural state, both initially and after irradiation, are shown in Fig. 2a and b, respectively, clearly showing a structure change from a fine crystalline state to an amorphous structure. Fig. 1c and d show another spot produced by a 500 ns pulse, characterized by a significant crystallized zone and a

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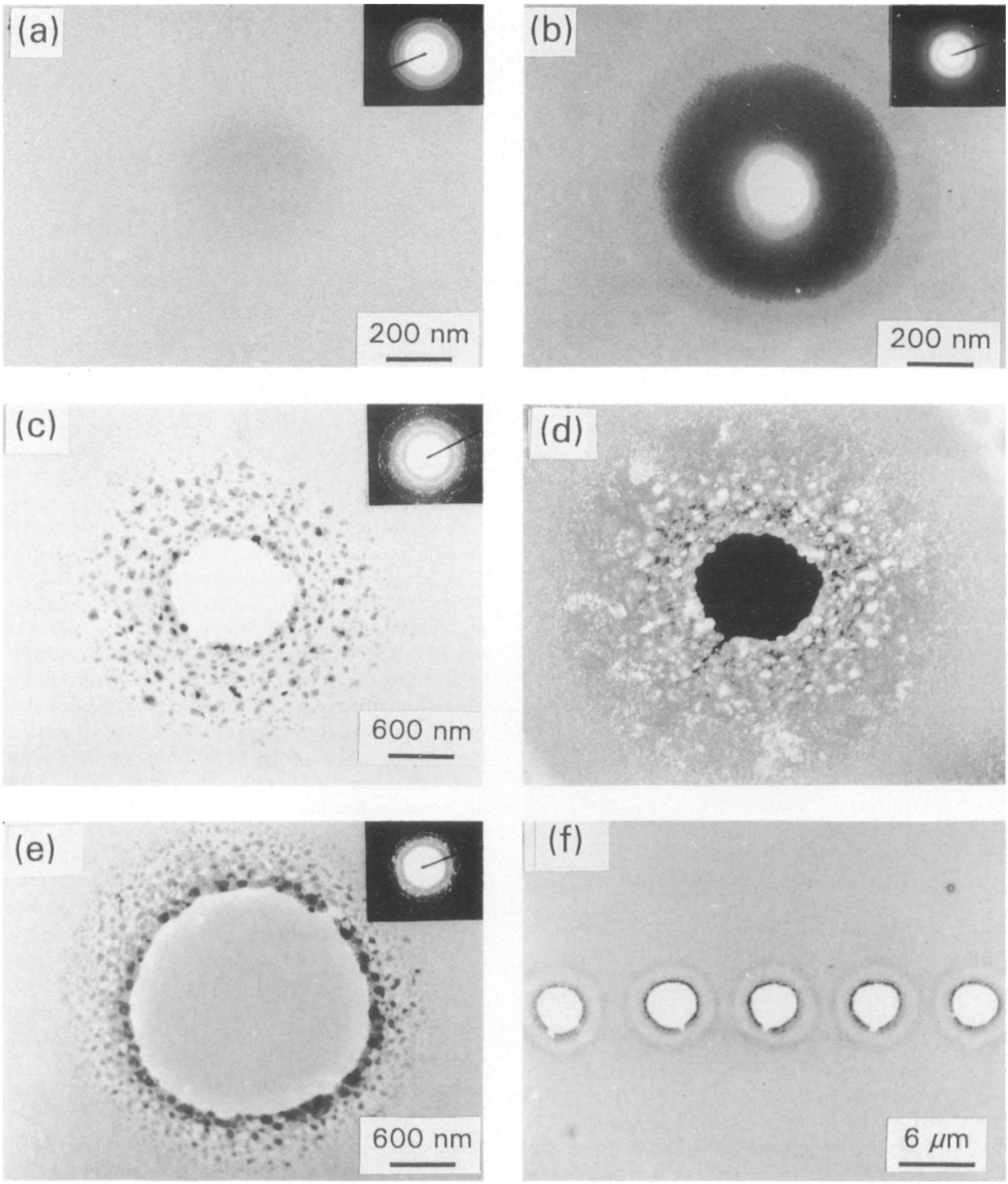

Figure 1 Electron micrographs and diffraction patterns of irradiated spots in evaporated $Al_{71}Cu_{29}$ film (initially an fcc solid solution) by a 17 mW laser with varying pulse length: (a) a faint mark without structure change, 100 ns pulse; (b) an amorphous spot with a damaged hole in the centre, 200 ns pulse; (c) spot with a significantly crystallized (Al + θ) zone surrounding the central damaged hole; (d) the dark-field image, 500 ns pulse; (e) spot with a similar crystallized zone to the above, plus a serious central damage, 1000 ns pulse; (f) the distribution of spot rows in the film.

large damage hole. The structure is determined from the diffraction patterns as aluminium and Al_2Cu (θ) mixture phases – the equilibrium state according to the phase diagram [8]. A further increase in pulse duration to 1000 ns, as expected, leads to an expansion of spot size with a large central damage hole. The phase is determined to be the same as in the 500 ns case.

Irradiation performance was also evaluated on the amorphous sample which was stripped from the cooled substrate. While employing a 14.5 mW pulse laser, a threshold pulse of about 200 ns is estimated. An interesting result was observed with a 300 ns pulse irradiation. As shown in Fig. 3, the whole spot, with a regular sphere-like shape, consists of a single crystal. According to the diffraction analysis, this crystal is a metastable structure with an fcc lattice ($a = 0.718$ nm) which had previously appeared in the thermally annealed case [7].

Therefore, it becomes evident that the resultant structure of the irradiated spots is a function of the laser parameter, i.e. the resultant structure can be

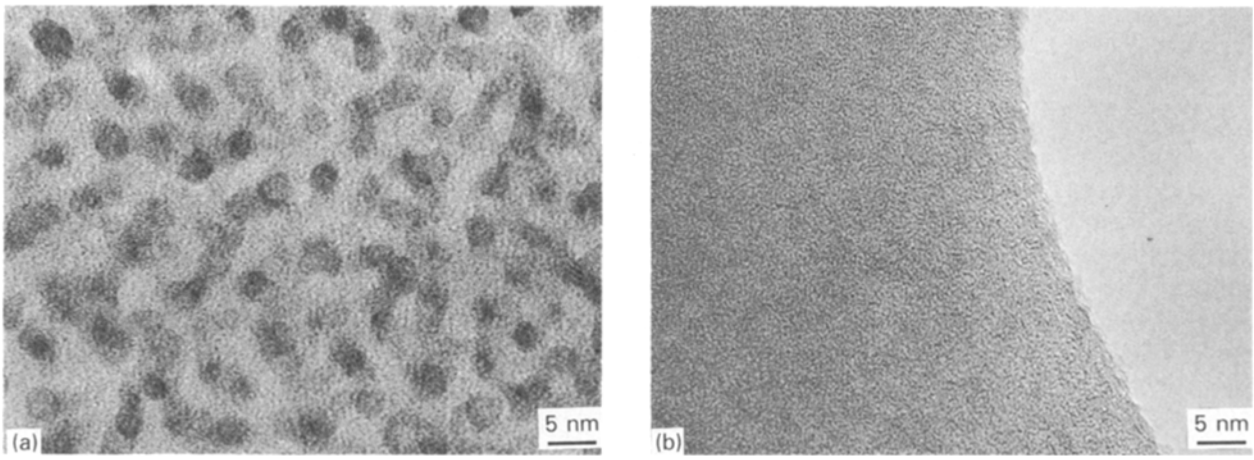

Figure 2 High resolution image of (a) uncooled evaporated film, showing fine crystallites, about 4 nm in size, distributed in the amorphous matrix (the structure is determined by the diffraction analysis as an fcc phase with $a = 0.396$ nm). Some {1 1 1} and {2 0 0} fringes are distinguishable; (b) amorphous spot (as in Fig. 1b) near the damage edge, no crystalline fringe detectable.

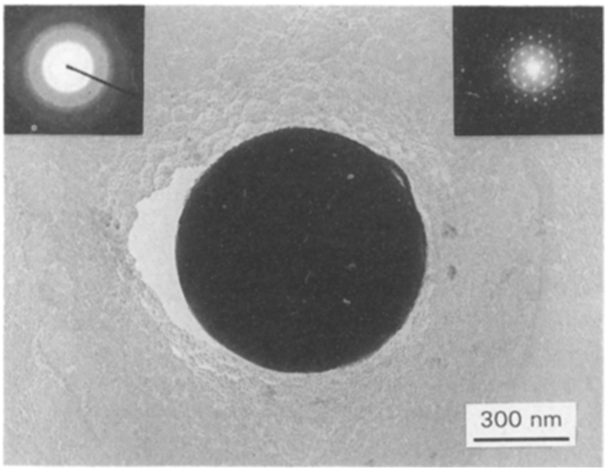

Figure 3 A sphere-shaped crystallized spot produced by a 14.5 mW, 300 ns pulse laser. Diffraction analysis indicates the structure of a single crystal with an fcc lattice (a typical pattern is shown at the top right). The surrounding structure is still amorphous as indicated by the top left pattern.

controlled by employing a suitable parameter. To understand this phenomenon, the kinetic process of the laser and materials interaction was considered with the help of computer simulation.

3.2. Kinetics of laser irradiation

There have been many theoretical calculations of the film's thermal response to the laser irradiation. We here use an equation proposed by Bartholomeuze [9] which was based on a one-dimensional heat flow model. It is assumed to fit a thin-film case. The necessary thermal property parameters of $Al_{71}Cu_{29}$ film used in the equation are given by the percentage sum of those of elements aluminium and copper.

Fig. 4a is a calculated temperature profile of the $Al_{71}Cu_{29}$ film response to the various laser pulses. The increase in peak temperature and widening of the heater region with the pulse duration is obvious. The temperature reaches over 1400 °C after a duration beyond 200 ns. This may explain the centre damage of the irradiated spot as shown in Fig. 1. That is, the high peak temperature in the centre can lead to not only melting of the materials, but also yield violent splashing, hence high tension or recoil pressure as well. The size of the hole may roughly represent this violently splashed region, while the spot can be regarded as the irradiation affected area. It should be explained that the peak temperature predicted here may be greater than in the real case, particularly in the long pulse case, as the heat transition during the phase change is neglected in Bartholomeuze's model. This deviation may also affect the calculated temperature profile with radial distance. Being aware of this, the simulation can be treated as a qualitative model.

The simulated cooling process of the 200 and 1000 ns irradiated cases is shown in Fig. 4b and c. According to this, the cooling down period is up to 10 ns in both cases, irrespective of their different initial temperatures, hence a cooling rate of about 10^{11} °C s^{-1} is estimated. With this extreme cooling rate, an amorphous phase would be favoured to form if the materials had been melted. The prediction is consistent with the experimental evidence from the 200 ns case, but deviates from the other longer pulse irradiation cases with the crystalline phases present. The question then arises: what causes the formation of crystalline structures in the other cases? We argue here that a non-melting crystallization mechanism may be employed to explain the phenomenon. As seen from Fig. 4a, the temperature rise with radius forms a continuous curve, from room temperature to the peak temperature. A certain region must exist where the elevated temperature is between the materials phase transition temperature (this could be a glass transition temperature if the initial state is amorphous, or a temperature to transform crystal 1 to crystal 2 if several crystalline states exist) and the melting temperature. The retention time for this elevated temperature, therefore, is of the scale of the pulse duration (hundreds of nanoseconds), and the crystallization or recrystallization may develop during that period. The subsequent rapid cooling after pulse irradiation will

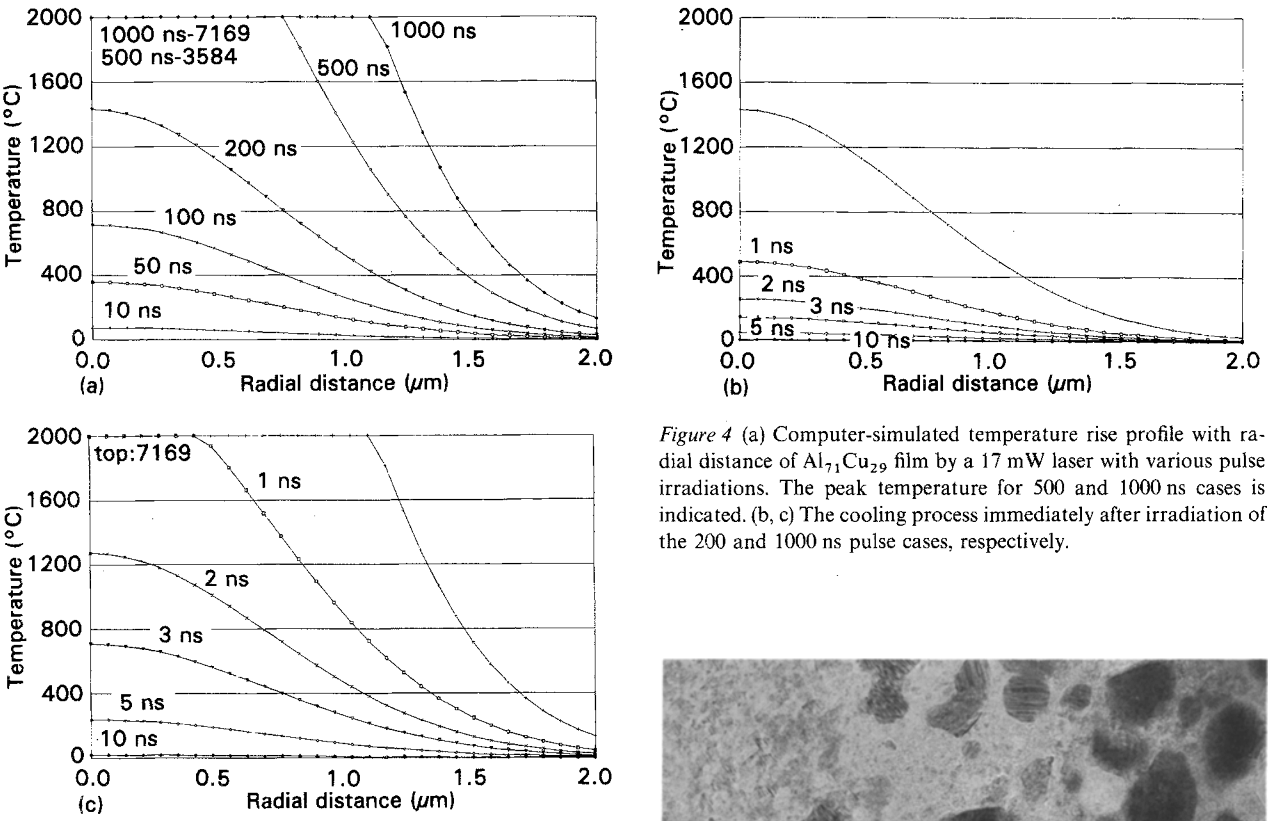

Figure 4 (a) Computer-simulated temperature rise profile with radial distance of $Al_{71}Cu_{29}$ film by a 17 mW laser with various pulse irradiations. The peak temperature for 500 and 1000 ns cases is indicated. (b, c) The cooling process immediately after irradiation of the 200 and 1000 ns pulse cases, respectively.

freeze this developed crystalline structure instead of the amorphous structure from the molten state. With this assumption, the whole resultant structure pattern of a long pulse irradiated spot would be expected as follows: an amorphous or high-temperature phase near the central melted area and a lower temperature or equilibrium crystalline phase in the surroundings (final structure depending on the pulse duration and the elevated temperature). Structural variation in each zone may also be possible because the temperature increase is not even, which may result in the various degrees of structure arrangement.

There is evidence to support the above assumption. Fig. 5a shows a higher magnification electron micrograph of the 1000 ns spot. Change in crystal size or morphology along the radius is obvious. Near the edge of the damage hole, an amorphous structure was revealed by the high-resolution image shown in Fig. 5b. This confirms the prediction that both amorphous and crystalline phases can be formed in different parts of the same spot.

Turning now to the interesting phenomenon of the case shown in Fig. 2, a temperature increase above the glass transition temperature, T_g, but below the melting temperature, T_m, across the centre is expected in this case. Supporting evidence is that there is no central damage in the spot, implying a gentle temperature rise. The crystallization is then developed during this 300 ns duration, and this condition seems able to form a metastable crystalline state, but not an equilibrium structure, which requires long-range atomic diffusion.

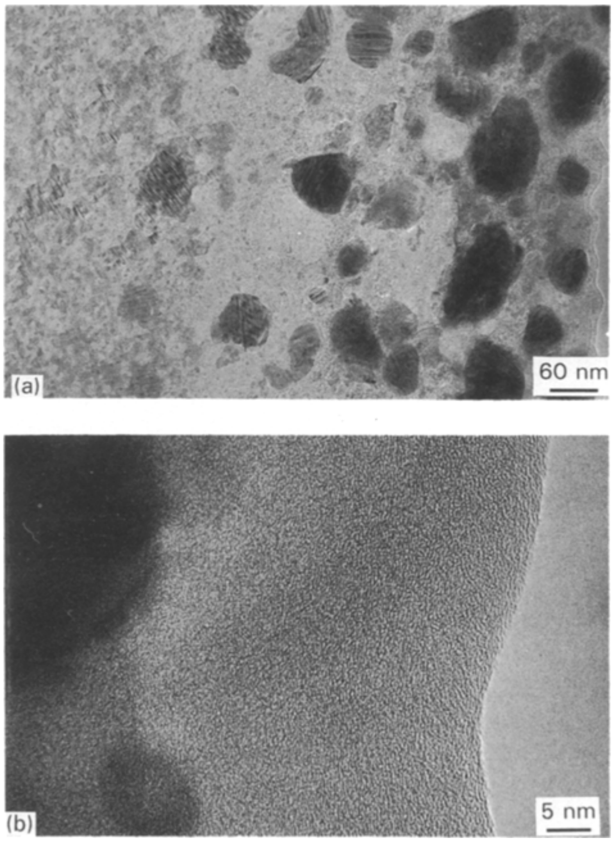

Figure 5 (a) High-magnification image of part of Fig. 1(e) spot, showing crystal-size variation along the radius. (b) High-resolution image near the damaged edge of the above spot, indicating the presence of an amorphous structure.

4. Conclusions

It has been shown that, for the evaporated $Al_{71}Cu_{29}$ film, both amorphization from the initial crystalline state and crystallization from the initial amorphous state can be achieved by using a suitable pulse laser. It has also been observed that amorphous and crystalline phases can both be present in different parts of the same irradiated spot. With the help of Bartholomeuze's equation, the kinetics of the film's response under pulse laser irradiation is discussed, leading to a proposal that amorphous or crystalline structures may be formed by a through-melting or non-melting mechanism. That is, a high cooling rate of about $10^{11}\,^{\circ}\mathrm{C\,s^{-1}}$ after the pulse laser irradiation, makes it possible to freeze any structure formed during the irradiation, e.g. an amorphous structure in the melted area and any form of crystalline state formed in the unmelted area. The resultant structure, therefore, is strongly laser parameter-dependent, especially when the material possesses several metastable states. The study lead to the following conclusions which may be constructive for understanding or finding fast speed phase-change materials.

1. Amorphization from a crystalline state by a pulse laser irradiation can be achieved by a through-melting process. It is necessary to utilize a suitable laser parameter in which the incident energy is over the material's melting threshold. To satisfy the demand for a high record/erase speed and minimum materials damage for optical storage, a shorter pulse compensated by a higher power is recommended.

2. The key to obtaining a homogeneous crystalline spot from the amorphous state is to produce a suitable temperature rise during the irradiation, to a temperature within the materials phase transition range. Therefore, the laser power must have a limitation to avoid over-heating of the materials. To shorten the pulse duration for the crystallization, materials with a fast crystallization speed are required. One approach, suggested by this work, is to use the amorphous to metastable crystalline phase transition which may exist in some metallic alloys. This phase transition should have no phase separation to satisfy the demand for both a fast phase-change speed and a long record/erase cycle.

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References

1. M. CHEN and K. A. RUBIN, Proc. SPIE-Int. Soc. Opt. Eng. (USA) Vol. 1078 (Optical Data Storage Topical Meeting, Los Angeles, CA, 17–19 Jan. 1989) p. 150.
2. TAKEO OHTA, M. UCHIDA, K. YOSHIOKA, K. INOVE, T. AKIYAMA, S. FURUKAWA, K. KOTERA and S. NAKAMURA, *ibid.*, p. 27.
3. YOSHIHITO, A. HISASHI, I. ISAO and M. HIROYUKI, *J. Appl. Phys.* **64** (1988) 1715.
4. H. YAN, Doctoral Thesis, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences (1989).
5. F. GAN and H. YAN, in Proceedings of C-MRS, International Symposium Meetings, Beijing, China, 1990, Vol. 4 edited by L. Huang (Elsevier-North Holland, Amsterdam, Netherlands, (1991) p. 445–50.
6. K. SUMIYAMA, Y. KAWAWAKE, Y. NAKAMURA, *Phys. Status Solids (a)* **96** (1986) K107.
7. H. YAN, F. GAN and D. HUANG, *J. Non-Cryst. Solids* **112** (1989).
8. M. HANSEN, "Constitution of Binary Alloys", (McGraw-Hill, New York, 1959).
9. B. J. BARTHOLOMEUZE, *J. Appl. Phys.* **64** (1988) 3815.

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