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Crystallization studies of electron beam-deposited telluride films

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This paper reports on the characterization of the crystallization of Ge–Te and Ge–Sb–Te films by several methods. The electron beam-deposited films, usually amorphous, were crystallized by oven-heating, laser irradiation and electron bombardment. Information on the micro-morphology and structure was collected by transmission electron microscopy and X-ray diffraction. The element binding states in the films were analysed by their X-ray photoelectron spectra. A unique f c c metastable structure as the crystallization product for a range of compositions was indexed. Attention was paid to the various effects of the different annealing methods. The mechanisms of phase transformation involving photo-induced reactions and thermal effects are discussed.

1. Introduction

Erasable and overwritable optical storage materials based on the mechanism of the amorphous–crystalline transition have been the subject of extensive research in recent years. The most promising materials for commercial application are still among certain tellurides which have shown an excellent cyclability [1]. However, owing to the emphasis on storage performance rather than materials science, the mechanism of crystallization, which plays a dominant role in the high-speed reversible phase-change process, is still unclear. It seems that, starting from the action of laser radiation, many physical effects are simultaneously or separately involved in the structure transition. The equilibrium phases resulting from the usual isothermal annealing procedure are unlikely to describe the state generated by a laser pulse. Such differences should be taken into account for a proper understanding of these transition processes, which is important for both theoretical and application developments.

In an attempt to elucidate further the mechanism of crystallization, this paper reports the characterization of the crystallization of Ge–Te and Ge–Sb–Te films by several methods.

2. Experimental

Ge–Te and Ge–Sb–Te films of various compositions were prepared using a Varian electron beam evaporation system. The source materials were GeTe, Sb_2Te_3 or mixtures of both compounds. The films were deposited on glass, silicon or rock salt substrates which were kept at room temperature during the depositions. The film thickness was controlled within the range 60–200 nm by using an Inficon XMS-1 quartz crystal monitor.

The as-deposited films, usually amorphous, were annealed by oven-heating in protective atmospheres at temperatures of tens of degrees Celsius above their crystallization points, usually 150–200 °C. A scanning laser microscope (SLM) with an argon-ion laser of wavelength 514 nm was also utilized to irradiate the films by way of both continuous scanning and short-pulse bombardment, and to detect the resultant effects.

Both the as-deposited and the annealed films were taken off their substrates for transmission electron microscopy (TEM) analysis. Information on the composition, morphology and structure evolution were collected by use of Philips 301 and 400 transmission electron microscopes. The annealing effects of the electron beam on the films were studied. In addition, the traditional X-ray diffraction method was utilized to investigate the crystalline structure.

X-ray photoelectron spectra of the films were collected with a Kratos XSAM 800 surface analysis facility in which the X-ray source was AlK_α (1486.6 eV). The element binding states in the films were analysed by the chemical shifts in their binding energies.

3. Results and discussion

All as-deposited compound films showed typical amorphous patterns in both electron and X-ray diffractions. They were easily crystallized by heating, laser irradiation or electron bombardment. The crystallization often brought about significant changes in the reflectivity and transmittance, e.g. the reflectivities of a sandwiched $GeSb_2Te_4$ film before and after the

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transition were 12 and 25%, respectively, which meant a relative contrast higher than 100%. For the same composition a pulse of duration 80 ns from a 830 nm laser diode could induce a visible crystallization.

SLM annealing experiments using the argon-ion laser beam with 2 mW power and a 0.5 numerical aperture (N.A.) objective deposited a power density of about 1.6×10^9 W m^{-2} on the films. According to structural analyses this transformed the as-deposited films into a crystalline state for most three-element compositions studied between GeTe and Sb_2Te_3. Fig. 1 shows the TEM diffraction pattern of this structure induced in the film of $Ge_{14}Sb_{29}Te_{57}$, which is near to the stoichiometric composition $GeSb_2Te_4$. There was little difference in the TEM diffraction patterns for a range of compositions on the pseudo-binary line, i.e. the crystalline state remained as shown in Fig. 1, although the rings were not as sharp in most other cases. The diffraction patterns from this phase were identified and indexed as a unique f c c structure. The lattice constant was derived to be $a_0 = 0.606$ nm. This single phase is actually a thermodynamically metastable state, in which the atoms of the different elements are randomly sited on the lattice. As a result the distortion of the lattice occurred easily, and therefore the diffraction rings were broadened. The previously reported hexagonal equilibrium structures [2] did not appear even in the higher-power cases, indicating that such structures may be of little importance with regards to the phase-change recording process.

Attention was paid to the variation between laser annealing and longer-duration annealing, e.g. oven-heating, which keeps the films at a stable temperature not far above their crystallization points, and electron beam irradiation with 100–120 keV accelerating voltage and high intensity, which also raises the local temperature to above the crystallization points. The metastable phase mentioned above could also be generated in the last two cases mentioned, i.e. oven-heating and electron beam irradiation, but accompanied by an obvious grain growth and element segregation which made the diffraction lines discontinuous and broad. A non-specific phase was often induced in these cases. The transition to the hexagonal structure of $GeSb_2Te_4$, which is the equilibrium phase, was finished by heating the samples at 300 °C.

The crystallization processes appeared to vary with the change in composition of the films. Fig. 2 shows an electron beam-irradiated area on GeTe films and the corresponding diffraction patterns. In this case crystallization happened by way of a so-called explosive and diffusionless transition, and induced a well-separated crystalline region. Compared with Fig. 2, the crystallization shown in Fig. 3, which is typical for most three-element films, seems to be a usual nucleation–growth type in which the sharp crystalline boundary did not appear and the grain sizes were affected significantly by thermoconductivity. Fig. 4 shows the effect of thermoconductivity on the crystallization processes of Sb_2Te_3 films 100 nm thick. It can be seen that there is an obvious difference in grain size between the two sides of a break in the specimen, with the upper side being connected with the copper grid. In addition, for those films of composition away from the pseudo-binary line, some dendritic crystalline grains first appeared in the amorphous matrix (Fig. 5) during electron irradiation, and a multiphase mixed structure finally formed. The crystalline morphology in the TEM images showed a gradual change from the irregular grains of GeTe (Fig. 2) to the equiaxed grains

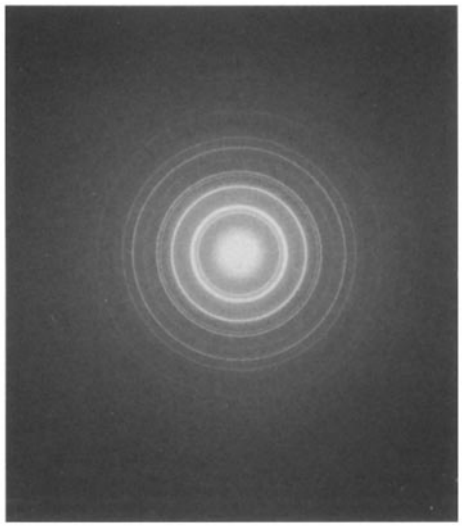

Figure 1 The transmission electron diffraction pattern of metastable f c c phase induced by an argon-ion laser (2 mW, NA = 0.5) in the Ge–Sb–Te system.

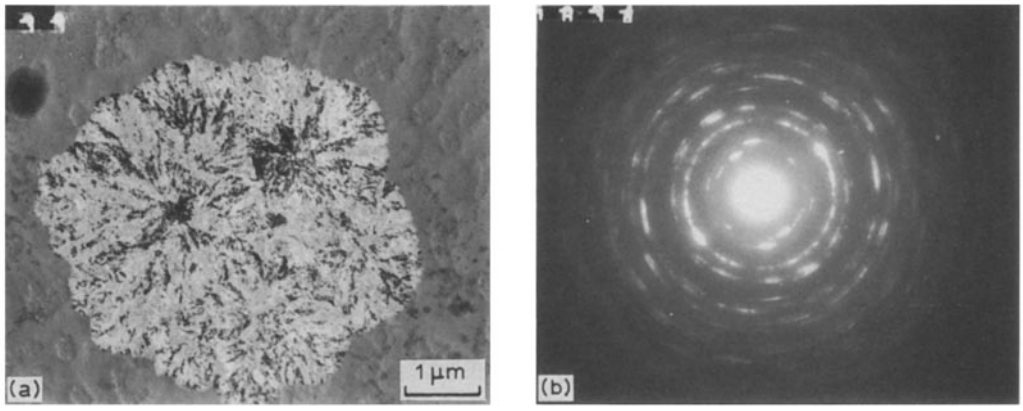

Figure 2 Crystallization of GeTe induced by electron beam irradiation (100 keV): (a) micromorphology showing the crystalline (white) area and (b) selected-area diffraction corresponding to the crystalline area in (a).

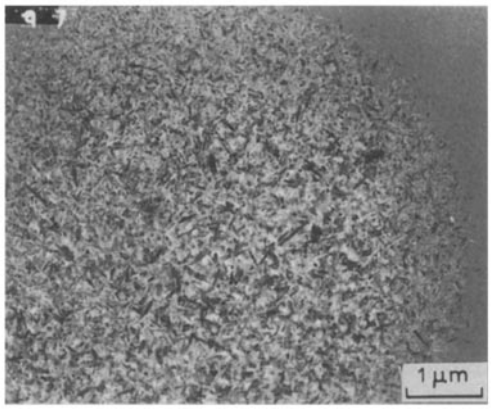

Figure 3 Micromorphology of crystalline area induced by electron beam irradiation (100 keV).

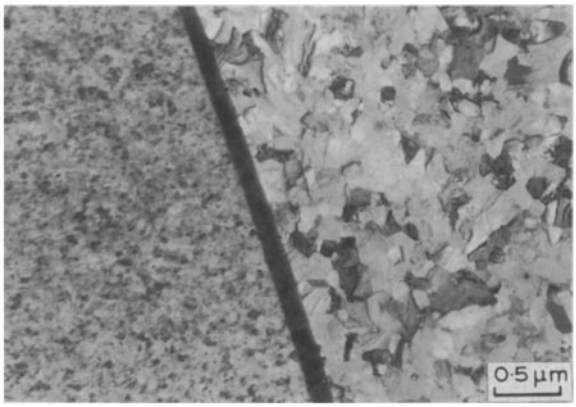

Figure 4 Crystalline morphology showing the difference between (left) disconnected and (right) connected area with copper grids in Sb_2Te_3 films.

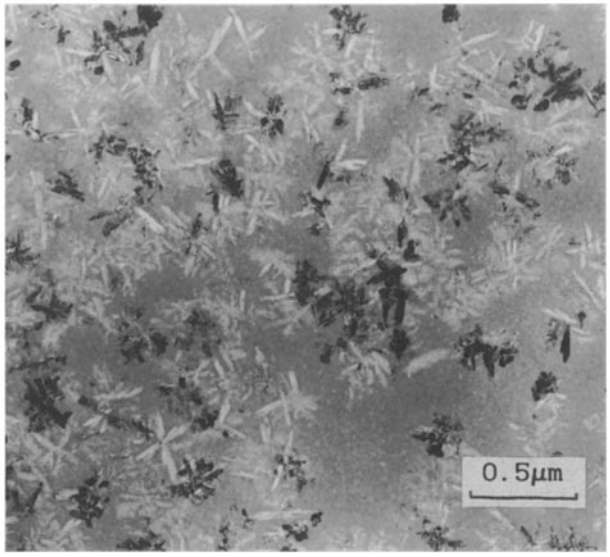

Figure 5 Dendritic crystals segregated from the amorphous matrix with composition away from the pseudo-binary line.

of Sb_2Te_3 (Fig. 4) with increasing Sb_2Te_3 content in the pseudo-binary films. A microstructure composed of parallel laths with periodic spacing of about 1.4 nm (Fig. 6) was observed in the crystalline grains which were created by long-time electron beam irradiation.

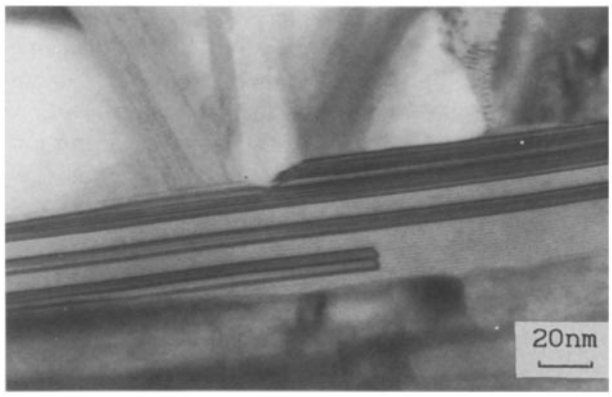

Figure 6 High-magnification image showing parallel layers with spacing about 1.4 nm, which is roughly equal to the periodical spacing of the hexagonal $GeSb_2Te_4$ structure.

X-ray diffraction of most crystallized films showed that the grain orientation in the films of practical thickness (< 100 nm) was of quite strong texture. This was not the case for thicker (about 200 nm) films.

X-ray photoelectron spectra showed that the obvious changes in the optical properties during the laser annealing were not accompanied by any significant changes in the element binding states, whereas changes in the binding energies did occur in the cases of thermal annealing. For the samples of GeTe, the peaks of Te-3d levels shifted by about 0.5 eV after heating at 200 °C, whereas the shift induced by laser scanning was < 0.1 eV. Similar results were obtained in the shallow levels (Te-4d). A comparison of the spectra of as-deposited, laser-annealed and thermally annealed GeTe films (Fig. 7) implied a closer similarity of laser-annealed states to the amorphous states than to the thermally annealed states. The very small differences between the levels before and after laser annealing may indicate that no drastic charge redistribution occurred. The peaks appearing in the higher-energy side of Te-3d levels were accounted for as the multiple chemical states of Te element in the films.

In the case of laser irradiation, energy is being supplied on a short timescale and with a spatial inhomogeneity, so the thermal gradients both in time and in space are very high. The product of this non-equilibrium transition is the metastable f c c structure, which should not be considered as just a middle stage of crystallization in the laser-recording process. This crystalline phase showed, especially for the compositions near to the stoichiometric compounds, not only distinct optical contrast from the amorphous state, but also good repeatability and no segregation. Depending on the compositional change and phase separation involved, various amorphous-to-crystalline transformations have been classified [3] as primary, polymorphic and eutectic. Laser pulse-induced crystallization in the Ge–Sb–Te system, through the formation of a unique f c c phase, showed an evident polymorphic characteristic even when the compositions were not at the equilibrium stoichiometry. On the other hand, the longer duration of energy supply gave the atoms more mobility to be sited at the positions with lower free energy in the cases of electron bombardment and oven-heating, in which the

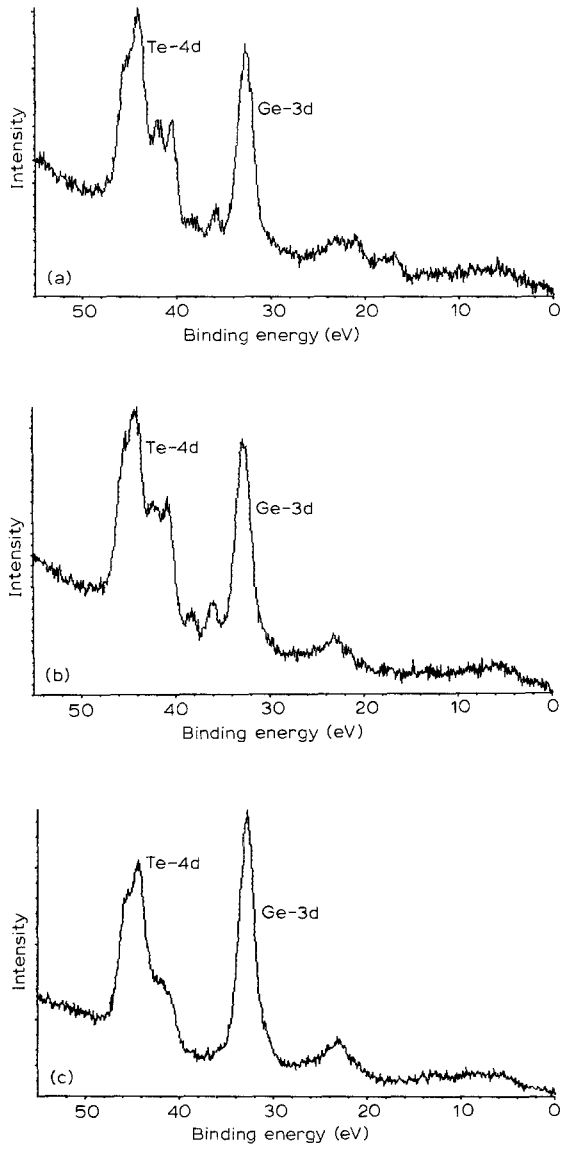

Figure 7 X-ray photoelectron spectra of GeTe films: (a) as-deposited, (b) laser-irradiated and (c) thermally annealed.

mechanism remains of primary type, i.e. nucleation and growth through long-range diffusion across the interfaces. There has been much experimental evidence supporting the temperature-dependent effect as a dominant factor in most above-microsecond scale cases.

In the present work, since the optical gaps of as-deposited films are between 1.1 and 1.55 eV [4], the absorption of laser photons through both band-to-band transition and free-carrier absorption should be significant. This could induce the leaping of a large number of electrons to the conduction band, and therefore the loosening of valence bonding. The free carriers created could then recombine and release energy when the laser irradiation ended. Consequently, the initiation of crystallization would be enhanced and the differences from solely thermal effects would be generated. The high phase-transition speed as well as X-ray photoelectron spectroscopy results could be attributed to the topological and chemical similarities between the metastable crystalline state and the original amorphous state, the formation of the former resulting from the short-range atomic rearrangement of the latter. This rearrangement was favoured by the photo-induced reaction. However, thermal effects would not be expected to be entirely excluded, especially for an indirect semiconductor such as telluride, in which a great number of phonons would be generated and transfer energy to the lattice. Some previous work [5] proposed a quantitative estimation in which the crystallization activation energy in the J–M–A equation was replaced by a lower value depending on the photon energy. Although complete quantitative information is not attainable, this may well be a valid explanation of laser-induced crystallization which is completed by a quite low incident power within short durations and repeated for millions of cycles. It is well known that the key problem of phase-change optical recording media is to incorporate a good thermal stability and a high crystallization speed. The double values of crystallization activation energy for photo-induced and solely thermal processes shows a promising way of achieving this.

4. Summary

Structural and morphological information about the crystallization of Ge–Sb–Te films were collected by several methods. A metastable fcc phase was shown to resemble the as-deposited amorphous structure and is considered to be the only crystalline state concerned in the optical recording process for media with a range of compositions. The photo-induced reactions contribute to the crystallization process and induce significant differences from long-timescale annealing, whereas thermal effects still function as the fundamental factor in the latter cases.

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