Time-resolved investigation of nanosecond crystal growth in rapid-phase-change materials for digital versatile disc

Y. Tanaka[1*], Y. Fukuyama[2], N. Yasuda[2], J. Kim[2], H. Murayama[2,6], S. Kimura[2], K. Kato[1], S. Kohara[2], Y. Moritomo[3], T. Matsunaga[4], R. Kojima[4], N.Yamada[4], H. Tanaka[1], T. Ohshima[1], and M. Takata[1,2,5]

[1.] RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan.
[2.] JASRI/ SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan.
[3.] The Graduate School of Pure and Applied Sciences, University of Tsukuba, Tennodai, Ttsukuba, Ibaraki 305-8571, Japan.
[4.] Matsutshita Electric Industrial Co., Ltd., 3-1-1 Yagumo-Nakamachi, Moriguchi, Osaka 570-8501, Japan.
[5.] Department of Advanced Materials Science , School of Frontier Science, The University of Tokyo, 5-1-5, Kashiwanoha,Chiba 277-8561, Japan.
[6.] Present address: Applied Chemistry, Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan.

*E-mail address: yotanaka@riken.jp

ABSTRACT

Understanding the mechanism of fast phase-change materials is one of the important topics in material science, hence numerous studies on the investigation of phase-change process as well as structural analysis of the crystal and amorphous phases have been reported. Nevertheless the mechanism of fast phase-change is still unclear due to the lack of detailed structure analysis, in particular time-resolved investigation during the phase-change. We developed a time-resolved X-ray diffraction apparatus coupled with *in situ* photoreflectivity measurement at SPring-8 synchrotron radiation facility, and succeeded in observation of the crystallization process in digital versatile disc (DVD) media. The time profiles of crystallization obtained by X-ray diffraction measurement were found to be consistent with the changes in photoreflectivity. Furthermore we found that the difference in crystallization time between $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ and $Ge_2Sb_2Te_5$ is ascribed to its characteristic crystallization process; X-ray diffraction profile of $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ shows sharpening during the crystallization process, whereas the peak width of $Ge_2Sb_2Te_5$ remained unchanged. Based on the experimental results, we propose a schematic model for the crystallization processes, being related to the difference in speed of the phase-change.

Key words: Synchrotron radiation, Time-resolved X-ray diffraction, $Ge_2Sb_2Te_5$, $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$

1. INTRODUCTION

A digital versatile disc (DVD) has now been a familiar memory device in our daily life when we record the relatively larger amount of information such as video and digital photographs. This is a result of the great efforts and developments paid for the progress in the device materials.[1] The idea of using an amorphous-crystal reversible phase-change phenomenon in chalcogenide materials for memory devices was proposed by Ovshinsky in the 1960s. The materials developed in early studies, however, had problems in the phase-change speed and the number of repetition cycle in the phase-change process for optical memories. Meanwhile, two landmark studies reported by Chen *et al.*[2] on GeTe and Yamada *et al.*[3] on Au-Ge-Sn-Te showed that a single crystalline phase is a key to producing reliable phase-change materials. These accelerated the development of new phase-change materials, leading to the discovery of GeTe-Sb_2Te_3 in 1987[4] and of $Ag_{11}In_{11}Sb_{55}Te_{23}$ in 1992[5]. The development of these materials has allowed us not only to produce rewritable compact discs, DVDs, and Blu-ray discs, but has also promoted the current rapid development of nonvolatile solid memories.

In contrast to the reliable performance of DVD media, the mechanism of rapid phase-change is still not fully understood. The crystal growth process in DVD media induced by laser irradiation has been investigated using various transmission electron microscopy, fluctuation electron microscopy, optical, electronic, and structural studies. Although recently developed DVD materials can complete their phase change with 20 ns laser irradiation, the real-time *in situ* observation of the crystal growth process in nanosecond time scale has never been reported. Real-time observation of the crystallization process in atomic scale will help us to reveal rapid phase-change phenomena. Then we developed a time-resolved X-ray diffraction apparatus coupled with *in situ* photoreflectivity measurement at the synchrotron radiation facility of SPring-8,[6] and reported on the crystallization process of $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$,[7] which are thought to exhibit different crystallization behavior. We here describe the measurement system and the result, together with the further development of the time-resolved X-ray diffraction system.

2. EXPERIMENTS

The purpose to construct the time-resolved diffraction measurement system mainly includes to know (i) the time constants of both crystallization and optical reflectivity changes, and (ii) crystallization behavior. We employed a femtosecond pulsed laser for crystallizing the amorphous samples, to measure the impulse response. The wavelength, pulse width, and pulse energy of the laser are 800 nm, 130 fs (FWHM), and 0.5 mJ/pulse, which is obtained with a Ti:sapphire laser system with a regenerative amplifier. For the measurement of the time constant of crystallization, we used a multi-channel scaler (MCS) to accumulate the X-ray photon counting signal detected with an avalanche photodiode located in the direction of the diffraction angle for the crystal phase. (Fig. 1(i)) The photoreflectivity was also monitored with a CW He-Ne laser (λ=632.8 nm) and a PIN photodiode. The time-resolution is determined by the detectors: 3.2 ns and 10 ns for the X-ray and photoreflectivity measurements, respectively. In order to investigate the crystallization behavior, we employed the stroboscopic method, in which pump and probe measurement using the 40 ps synchrotron X-ray pulse and the synchronous femtosecond laser pulse was conducted to obtain the transient X-ray diffraction profile with an imaging plate (Fig. 1(ii)).

The DVD samples were prepared by depositing $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ on a SiO_2 glass substrate (12 cm diameter and 0.6 mm thick) with a 2-nm-thick 80 mol% ZnS-20 mol% SiO_2 cap layer. The thickness of the sample was 300 nm, which gave sufficient X-ray diffraction intensities for structure characterization and sufficient stability of the amorphous phase to avoid spontaneous crystallization.

Repetitive measurement is required because the diffraction intensity for one shot was too weak to obtain the profiles with high time resolution. Since the sample thickness is different from that of the commercial disc, the condition of laser irradiation was optimized for crystallization. Therefore the sample was rotated to give a virgin sample for every measurement, as shown in Fig.2. The repetition rate is determined in consideration with the rotation speed of the disc and the X-ray beam size on the sample, as, $v(m/s) > f(Hz) \cdot s(m)$, where the v, f, and s are the moving speed, the repetition rate, and the X-ray beam diameter, respectively. In the experiment, we set $v = 8 \times 10^{-4}$ m/s, f = 5 Hz, s(vertical) = 5×10^{-5} m, s(horizontal) = 1.5×10^{-4} m, and the laser beam diameter was 100×300 μm (h $\times$ v). Since the smaller beam size and high repetition rate save the sample disc area and the measurement time, an X-ray microbeam technique was also applied to the experiment to obtain 3 micron X-ray beam size with a Fresnel zone plate.

The experimental setup at the beamline 40XU of SPring-8 is schematically illustrated in Fig. 2. The illustration shows the case of (ii) pump/probe measurement using the X-ray microbeam. The timing control between the pulsed laser and synchrotron radiation was achieved by synchronizing the laser to the RF (radio frequency) master oscillator of the synchrotron radiation accelerator. The time interval between them was controlled by shifting the RF signal phase with high precision of 3 ps.[8] For the measurement of (i), an imaging plate is replaced by an avalanche photodiode, and synchronization circuit is removed. The results of time-resolved photoreflectivity (see the lower right part of Fig. 2), time-evolution of Bragg diffraction intensity, and the stroboscopic measurement of X-ray diffraction profile are shown in the following section.

3. RESULTS & DISCUSSION

3.1. Time-resolved photoreflectivity

The time-resolved photoreflectivity profiles of 300-nm-thick $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ samples are shown as red curves in Fig. 3. A sharp negative peak can be observed at around 20 nsec in the photoreflectivity profiles of both $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$. Although the origin of the negative peak is still unclear, we surmise that decrease in the photoreflectivity may be due to the roughness of the sample surface transiently induced by femtosecond laser irradiation, because such a decrease was not observed on the rear side of the samples. Both profiles exhibit a rapid increase in the photoreflectivity between 100 and 200 ns. Wei and Gan[9] reported the change in photo reflectivity of a 30-nm-thick $Ge_2Sb_2Te_5$ film deposited by dc-magnetron sputtering and found three stages for the crystallization: an onset stage (~40 ns), a nucleation stage (~120 ns), and a growth stage (~140 ns). These stages can be observed in the photoreflectivity profile of $Ge_2Sb_2Te_5$; an onset stage of ~100 ns, a nucleation stage of ~200 ns and a growth stage, as observed in the second-order derivative of the reflectivity change (green lines in Fig. 3), whereas $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ does not show a distinct onset stage and nucleation stage between 100 and 200 ns.

3.2. Time-evolution of Bragg peak intensity

Time-profiles of the X-ray diffraction intensity of Bragg peaks (black and blue lines) show good accordance with those of the photoreflectivity profiles (red lines), as shown in Fig. 3. Furthermore, the slope in the X-ray diffraction profile of $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ is steeper than that of $Ge_2Sb_2Te_5$, indicating that the time constant of crystallization in $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ is smaller than that in $Ge_2Sb_2Te_5$. The X-ray diffraction data were fitted by a linear function, and the times which the function exhibits 0% and 100 % of diffraction intensity change, were defined as start and end time, respectively: the start and the end times are 90 ± 1 ns and 273 ± 1 ns for $Ge_2Sb_2Te_5$, and are 85 ± 1 ns and 206 ± 1 ns for $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$, respectively. The diffraction intensity changes exponentially and stops at approximately 300 ns, which means that the crystallization of the amorphous phase in both $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ is almost finished within 300 ns. Consequently, although the thickness of the sample in our study is larger than that in commercially available devices, our results are evidence of a strong relationship between X-ray diffraction intensity and the photoreflectivity of the phase-change materials, *i.e.,* the structure and the electronic properties.

3.3. Snapshot of X-ray diffraction pattern

The snapshots of X-ray diffraction pattern were taken during the crystal growth with stroboscopic method. From the time-evolution of Bragg peak intensity as described in *3.2*, the delay times, τ, between the laser pulse and X-ray pulse were determined. Figure 4(a) shows the diffraction patterns obtained from the stroboscopic method for a 40 ps snapshot. Since the intensity of each diffraction peak shows a uniform time-dependent increase, there is no crystal-crystal phase transition in $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ during the crystal growth. However, the positions of the diffraction peaks shift to a higher angle corresponding to a lattice parameter shrinkage of about 1% due to the time-dependent temperature decrease. We estimated the grain sizes from the line width of Bragg reflection, as shown in Fig. 4(b), as 69 ± 1 nm at 300 ns to 71 ± 1 nm at 1 µs for $Ge_2Sb_2Te_5$ and from 58 ± 1 nm to 65 ± 1 nm for $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$. In $Ge_2Sb_2Te_5$, the grain size is nearly constant (=70 nm), while the grain size significantly increases up to 1 µs in $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$. It is remarkable that the volume fraction of the crystal phase is almost saturated at 300 ns (see Fig. 3). Thus these observations suggest the coalescence of the crystal domains after 300 ns.

3.4. Crystallization process

From the experimental findings reported in *3.1-3.3*, we propose models for the crystallization processes of $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$. In the case of $Ge_2Sb_2Te_5$, nucleation takes place in the whole area in the amorphous phase after laser irradiation, and the number of newly formed crystallites of ～70 nm diameter increases during the cooling process until 300 ns. The crystal growth is then disturbed by the impingement of crystallites with each other. On the other hand, the nuclei of $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ can immediately transform to smaller crystallites (<< 60 nm), which form domains. These domains are enlarged by edge-growth crystallization and the crystallites coalesce

at the final stage (300 ns~) of crystallization in $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$. These proposed schematic models are consistent with the TEM pictures, in which $Ge_2Sb_2Te_5$ has a grainy texture filled with 100-nm-size grains, whereas $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ has a fine texture.

4. CONCLUSION

We constructed a time-resolved X-ray diffraction measurement system combined with *in situ* photoreflectivity probe at the synchrotron radiation facility of SPring-8, and succeeded in observing the crystal growth in DVD materials. The combination of time-resolved X-ray diffraction and photoreflectivity measurement has showed the strong relationship between the changes in structure and photoreflectivity of $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$, which suggests a difference between their crystallization processes. The X-ray diffraction profiles obtained by the X-ray snapshots indicate that the rapid phase change in crystallization is achieved through the nucleation-grainy crystal growth stages for $Ge_2Sb_2Te_5$, and the fast production of crystallites for $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$. Our findings suggest that the crystal growth mechanism is governed by a nanoscale phase-change mechanism, hence the real-time observation with X-ray diffraction is important in development of the faster phase change devices. We have also conducted the 1 kHz-repetitive measurement in combination of a few micron-sized X-ray microbeam, in order to obtain the clear snapshot of X-ray diffraction profile with higher signal-to-noise ratio. This showed the line profile change in earlier stage of crystallization, and also enabled quantitative estimation of lattice constant change *etc*. We are now discussing on the obtained results and hope to report some of the results at the meeting.

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Biographies

Yoshihito Tanaka is a Senior Research Scientist at SPring-8 Center of RIKEN Harima institute, and the Visiting Professor of Kwansei Gakuin University. Doctor of Science degree was given at the University of Tokyo in 1992, the thesis of which is on the energy transfer dynamics in gas phase samples by using laser spectroscopy. At the RIKEN Institute located in Wako-city, Saitama, picosecond time-resolved laser spectroscopy using nonlinear optical effect was employed for surface dynamics research. In 1997, he moved to the Harima Institute located in Hyogo Prefecture,

and constructed picosecond timing synchronization system between femtosecond pulsed lasers and synchrotron radiation pulses for time-resolved X-ray measurement. Using this system, he succeeded in watching the picosecond lattice dynamics in semiconductors, and photochromic organic crystals. The research project of "X-ray pinpoint structural measurement for nano-materials and devices" started in 2004, giving him a great chance to meet the specialist on the optical memory media, and he has been in charge of the development of the time-resolved measurement technique for investigation on changing stage in the phase transition.

His recent interest is femtosecond time-resolved measurement using X-ray free electron lasers, which will appear in SPring-8 cite in a few years. This will make it possible to watch the earlier stage of transition in fast phase change materials.

The academic research affiliations are the Physical Society of Japan, the Japan Society of Applied Physics, and the Japanese Society for Synchrotron Radiation Research.
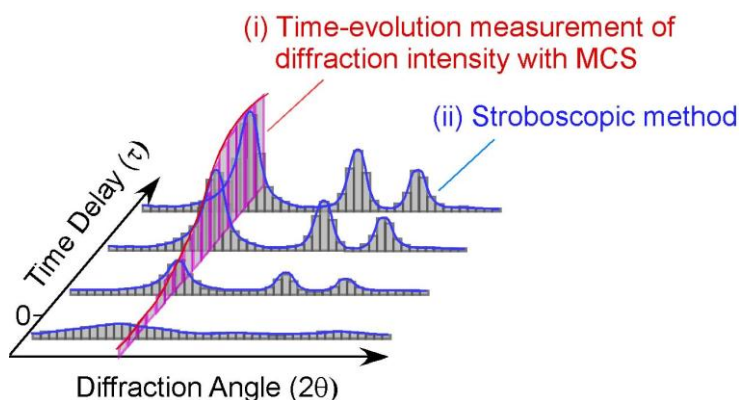

Fig. 1.   Schematic illustration of time-resolved X-ray measurement methods.
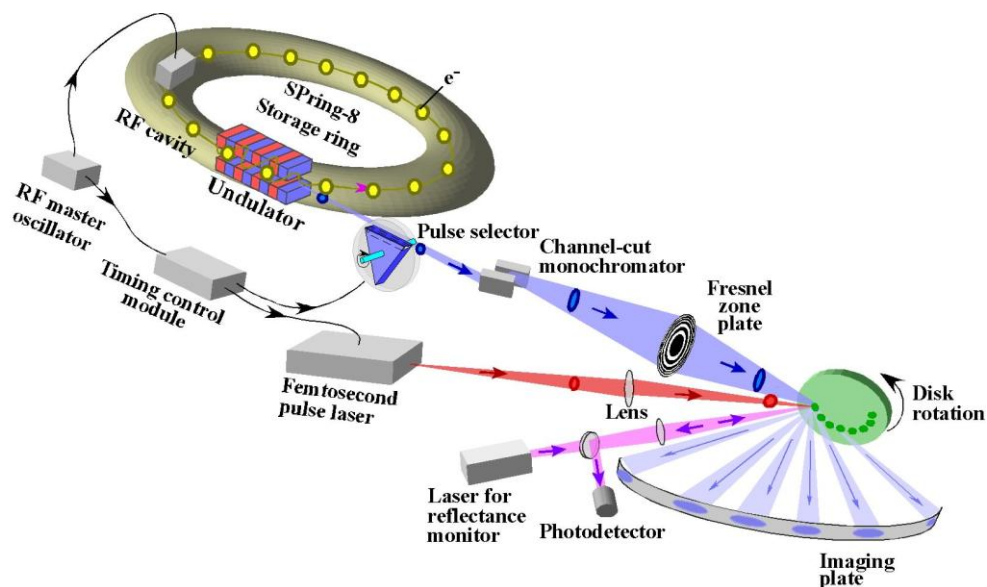

Fig. 2.   Schematic illustration of the time-resolved measurement system developed for investigation on fast phase change in DVD materials.
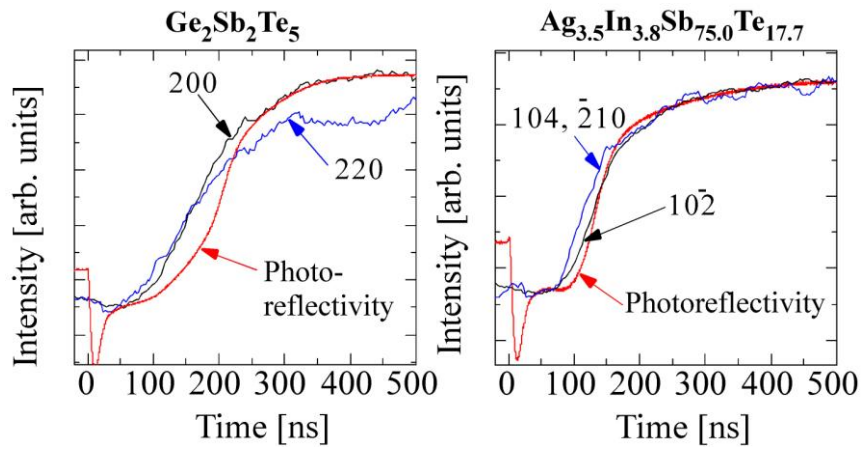
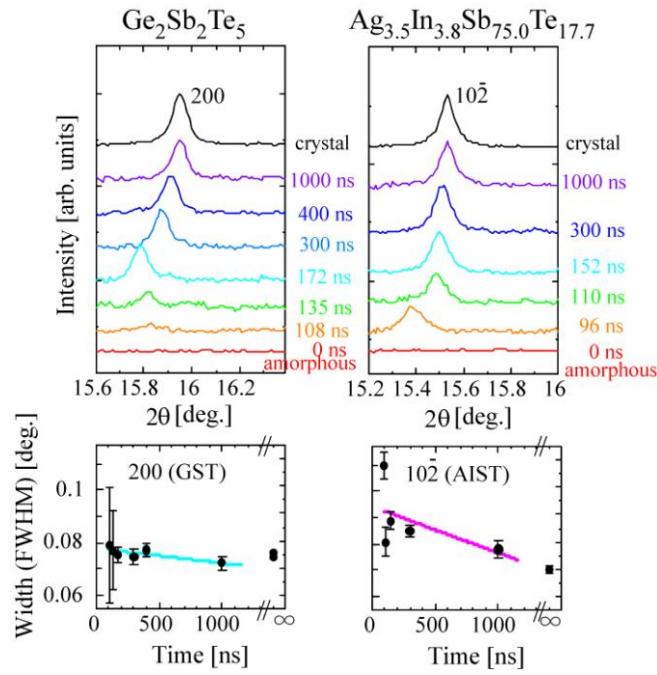Fig. 3.   Time-evolution of the photoreflectivity and X-ray diffraction intensity.

Fig. 4.   Snapshots of X-ray diffraction patterns and the changes in peak width.