Time-Resolved Investigation of Nanosecond Crystal Growth in Rapid-Phase-Change Materials for Rewritable Digital Versatile Disc

The rapid phase-change mechanism in DVD-RAM (digital versatile disc-random access memory) materials has been investigated using the "X-ray pinpoint structural measurement" system developed at the high flux beamline **BL40XU**. The measurement system has been constructed with support of the Core Research for Evolutional Science and Technology (CREST) project, organized by the Japan Science and Technology Agency (JST). The aim of the project is to accomplish picosecond time-resolved X-ray diffraction experiment using a submicrometer-scale beam. This is why the project is termed "pinpoint." Specialists in accelerator science, laser physics, X-ray optics, diffraction physics, crystallography, and chemistry have joined this project from several institutes, i.e., JASRI/SPring-8, RIKEN SPring-8 Center, Panasonic Corporation, Tsukuba University and University of Hyogo. The target specifications of the X-ray pinpoint structural measurement are ~100 nm spatial resolution and ~40 ps time resolution [1]. To ensure the precision of the time resolution, we devised a new precise timing control system, which allows us to keep the timing accuracy within 5 picosecond in any case [2].

In rewritable DVDs, such as DVD-RAM and DVD-RW, information is written to the phase-change materials composed of the alloys of Ge, Sb and Te, or those of Ag, In, Sb and Te, by changing their phase between amorphous and crystalline states using submicrometer-sized laser irradiation. Although recently developed DVD materials can complete their phase change with 20 ns of laser irradiation, the real-time *in situ* observation of the crystal growth process in the nanosecond time scale has never been reported. We therefore conducted a time-resolved X-ray diffraction experiment coupled with *in situ* photoreflectivity measurement using the X-ray pinpoint structural measurement system to study the crystallization processes of $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ [3], which are thought to exhibit different crystallization behavior. To reveal the crystallization process of the amorphous phase in these rapid phase-change materials, it is necessary to know (i) the time constants of both crystallization and optical reflectivity changes, and (ii) the crystallization behavior. Thus, we employed avalanche photodiode (APD)/multi-channel scaling (MCS) measurement with

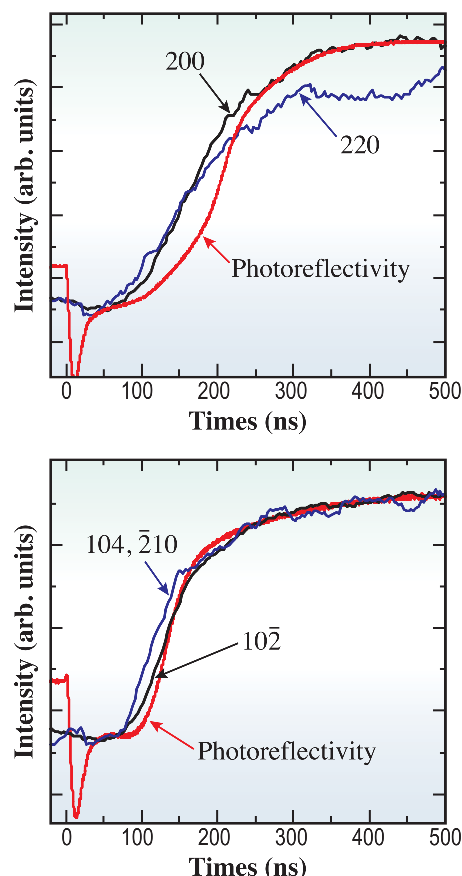

Fig. 2. Time evolution of photoreflectivity and X-ray diffraction intensity.

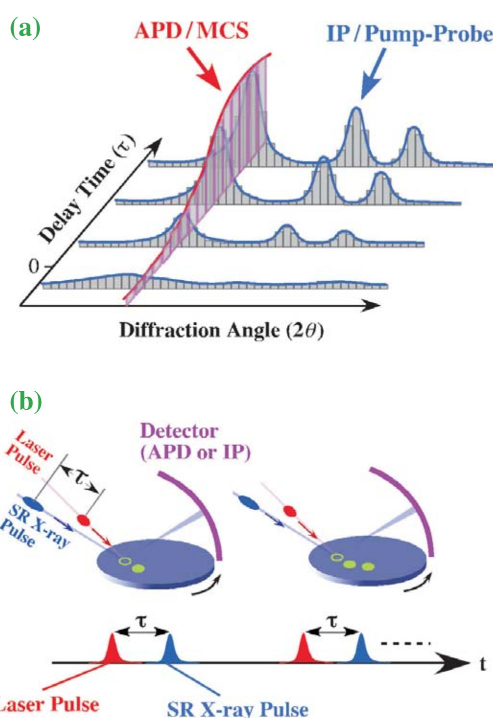

Fig. 1. **(a)** Schematic diagram of APD/MCS and IP/pump-probe measurement and **(b)** scheme of DVD rotating system and the time chart of pump-probe measurement.

a time resolution of 3.2 ns coupled with photoreflectivity measurement for (i) and imaging plate (IP)/pump-probe measurement of a time resolution of 40 ps for (ii), as schematically shown in Fig. 1(a). Figure 1(b) shows the experimental method and the time chart for pump-probe measurement using 40 ps X-ray pulses and synchronous femtosecond laser pulses. 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.

Figure 2 shows time dependence of the X-ray diffraction intensity of Bragg peaks (black and blue lines) together with the photoreflectivity profiles (red lines), measured by APD/MCS measurement. These show good agreement, which proves the close relationship between X-ray diffraction intensity and the photoreflectivity of the phase-change materials, i.e., between the structure and the electronic properties.

From the intensity profile measured by the APD/MCS method, the delay times, τ, were determined for the IP/pump-probe method. Figure 3(a) shows the diffraction patterns obtained by the IP/pump-probe method for a 40 ps snapshot. Since the intensity of each diffraction peak has a uniform time-dependent increase, there is no crystal-crystal phase transition in $Ge_2Sb_2Te_5$ or $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ during the crystal growth. We estimated the grain sizes from the peak width of Bragg reflection, as shown in Fig. 3(b). 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 noteworthy that the volume fraction of the crystal phase is almost saturated at 300 ns (see Fig. 2). Thus these observations suggest the coalescence of the crystal domains after 300 ns.

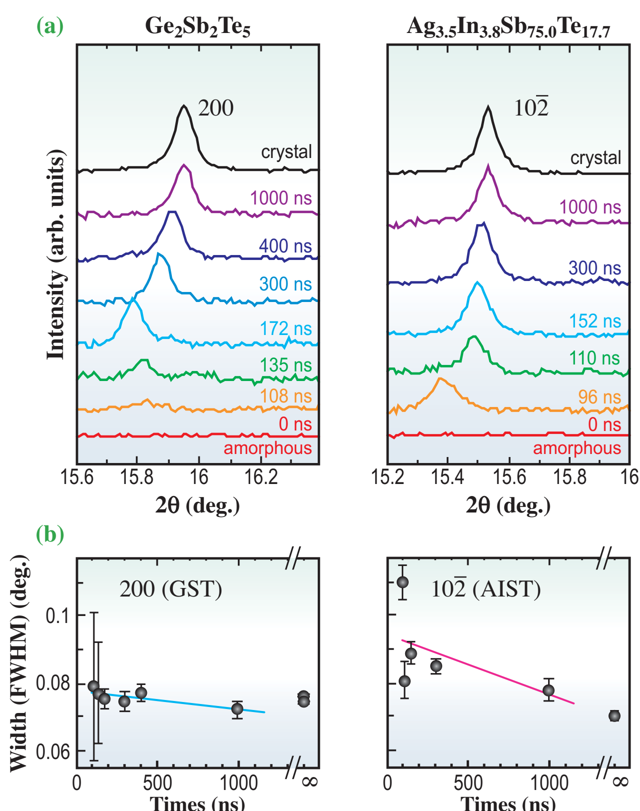

Fig. 3. **(a)** Snapshots of X-ray diffraction patterns and **(b)** changes in peak width.

On the basis of the above experimental findings, we propose schematic models for the crystallization processes of $Ge_2Sb_2Te_5$ and $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$. In $Ge_2Sb_2Te_5$, large crystal grains form over the entire volume of the material from the moment the process starts, while in $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$, the process begins with the formation of small crystallites in different parts of the material, which gradually grow and merge to form larger grains.

The X-ray pinpoint structural measurement system is now close to completion. The system, which is an integration of the time-resolved experiment and microbeam technique [4], will be applied to investigate, for example, photo-induced phase transition, and structural change under applied AC electric field, as well as the phase change of DVD materials.

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