Laser pump and synchrotron radiation probe microdiffraction of $Ge_{10}Sb_{90}$ phase-change nanometer-sized dots

Digital versatile discs (DVDs) and Blu-ray discs are two of the most convenient optical storage devices for large amounts of information such as that in videos and digital photographs. These storage devices were realized owing to the extensive efforts and developments that have been made in the progress of phase change (PC) technologies. Reportedly, practical PC material films complete the reversible structure changes with 20 ns laser irradiation. However, the continuous development of PC devices is still a major concern: the aim is to realize a new class of storage devices with a large capacity and a high recording rate corresponding to the huge amount of digital data explosively increasing yearly. Among many candidates, the combination of PC nanometer-sized dots (nanodots, hereafter) and near-field optics has noticeably high potential (ideally more than 100 times larger capacity), since it may overcome the issues regarding the optical diffraction limit. One essential point to note here is whether the crystallization speed, which limits the recording rate, will be maintained for the nanodots.

To examine this point, it is crucial to precisely observe the crystallization process of the nanodot materials in real time. We previously developed a time-resolved X-ray pinpoint measurement system to observe the structural changes of PC materials on a nanosecond time scale using synchrotron radiation (SR) at beamline **BL40XU** [1,2]. The system coupled with an *in situ* optical reflectivity monitor demonstrated a strong correlation between crystal growth and optical reflectivity [1]. Using this system, we successfully observed the crystallization processes of some PC material films with a rather large thickness of 300 nm on a SiO_2 glass substrate. Nevertheless, doubt remained as to whether the observed crystallization behavior would be the same as that of a much thinner PC material film in real recording devices or that of future nanometer-sized dot materials, where the diffraction intensity will be lower and the background noise will increase owing to additional layers, e.g., a metal layer beneath the PC material layer. We therefore developed a new experimental system for laser-pump and SR-probe microdiffraction (Fig. 1) [3] by combining (i) a pump laser system (pulse width: 300 ps; repetition rate: 1 kHz), (ii) a highly brilliant focused microbeam with peak-energy width ($\Delta E/E \sim 2\%$) accomplished by focusing helical undulator radiation without monochromatization, and (iii) a precise sample disc rotation stage with a position

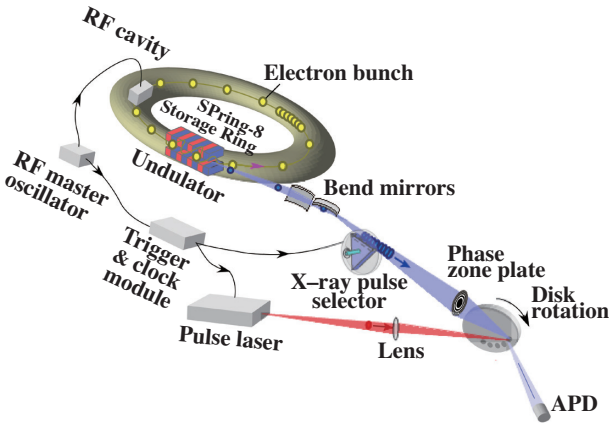

Fig. 1. Schematic of setup for laser-pump and synchrotron radiation (SR)-probe microdiffraction. The sizes of the pump laser and probe SR beams on the sample surface were optimized according to the sample shape: approximately 10 × 100 μm^2 (laser) and 1.98 × 16.6 μm^2 (SR).

feedback system for repetitive measurements. We then applied the system to observe the laser-induced structural changes of 50-nm-class $Ge_{10}Sb_{90}$ nanodots embedded in a thermally managed multilayered structure (Fig. 2) [4].

The nanodot specimens were fabricated by successively sputtering multilayers on a patterned glass disc substrate with a diameter of 64 mm (HOYA Corp., Japan); on the glass substrate, UV-resin nanopillars with a diameter of 50 nm and a height of 100 nm were formed with a 100 nm pitch using the nanoimprinting technique. The layer stack was designed to imitate the structure of a commercial phase-change optical disc; it was optically optimized to exhibit a large change in reflectivity that corresponds to the amorphous-to-crystalline phase transition. Sb-based phase-change alloys, including $Ge_{10}Sb_{90}$, were characterized by growth-dominant crystallization processes owing to their relatively low nucleation rates but high growth rates [5]. To overcome the low nucleation rates, pure Sb layers were inserted as seed layers, which were crystallized during or immediately after deposition and serve as a precursor for the $Ge_{10}Sb_{90}$ layer. A silver layer with a thickness of 40 nm was used to enhance optical absorption in the $Ge_{10}Sb_{90}$ layer and also to protect the resin pillars from thermal damage. The multilayers were deposited almost exclusively on top of the nanopillars to successfully form nanodot recording elements.

Because the size of the SR probe beam was large (approximately 1.98 × 16.6 μm^2) compared with that of the nanodots (φ50 nm for each), we simultaneously observed diffractions from approximately 1200 to 1300 nanodots with one laser shot. Furthermore, since the diffraction intensity from one shot was very low, we compiled cumulative diffraction data by changing the measuring position on the sample for every shot.

Figure 3 shows the results of time-resolved diffraction intensity measurements of the 012$_H$ peak, the most intense peak, of crystalline $Ge_{10}Sb_{90}$ with rhombohedral symmetry *R*-3*m* resembling pure Sb. As seen in the figure, we could successfully detect the structural change from an amorphous state to a crystalline state as the variation in diffraction intensity on the nanosecond scale. All diffraction intensity profiles began to increase with a delay of approximately 70–100 ns and saturated at approximately 150 ns after laser pumping for 300 ps. By comparing curves (a) to (d), it is seen that the time delay before the start of crystallization becomes slightly shorter as the laser power decreases from (a) to (d). This indicates that setting the pumping laser power to slightly above the threshold of crystallization is effective for minimizing the crystallization time.

In conclusion, we successfully revealed the rapid crystallization of 50-nm-class $Ge_{10}Sb_{90}$ nanodots embedded in a multilayered structure in response to a short laser excitation of not more than 300 ps. This indicates the high potential of the nanodot material for use in next-generation ideal 'green data storage' systems with ultrahigh density and high recording speed.

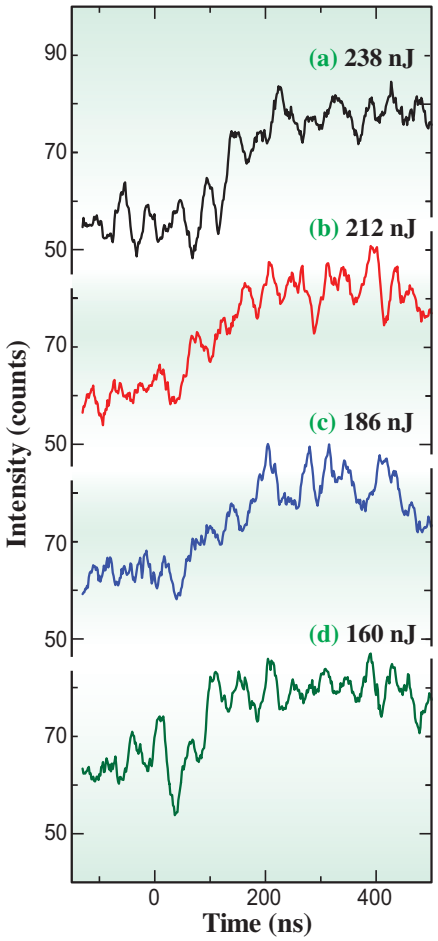

Fig. 3. Experimental results of the time-resolved diffraction intensity due to crystallization of the $Ge_{10}Sb_{90}$ nanodots with various pump powers of **(a)** 238, **(b)** 212, **(c)** 186, and **(d)** 160 nJ. Each curve was obtained by accumulating data from approximately 100,000 shots and plotted by averaging ten adjacent data, meaning that the time resolution was 16 ns, to smooth the curves.

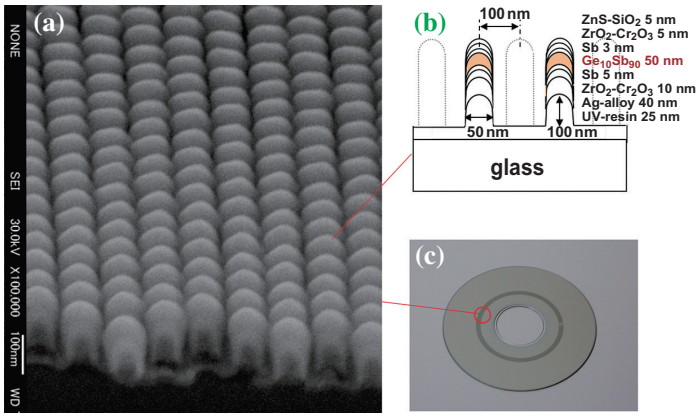

Fig. 2. SEM photograph **(a)** and schematic of cross section **(b)** of nanodot specimens. Approximately 2.4 × 10^{10} nanodots were formed in a zone (φ33.0–35.4 mm) on a sample disc **(c)**.

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