Crystallization Study of Reamorphized-$Ge_2Sb_2Te_5$ Sandwiched by Dielectric Films

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ABSTRACT

Reamorphized marks (1 μm diameter, occupying a quarter of the total area) were prepared in crystalline $Ge_2Sb_2Te_5$ layer of an optical disc sample, and its crystallization temperature and activation energy were evaluated. The obtained values were compared with the ones of as-deposited $Ge_2Sb_2Te_5$ that has the same layer-stacking structure. The crystallization temperature decreased from about 166 ˚C to 131 ˚C, and the activation energy from 3.4 eV to 2.3 eV when the reamorphized $Ge_2Sb_2Te_5$ was crystallized. A direct comparison of the two states confirms that crystallization properties are dependent on the reamorphized mark condition and on the surrounding crystalline medium.

Key words: $Ge_2Sb_2Te_5$, amorphous, reamorphized, as-deposited, crystallization temperature, activation energy

1. INTRODUCTION

Phase change materials, e.g., $Ge_2Sb_2Te_5$, are now used for the rewritable optical disc media, and will be for one of the future electrically-switched random-access-memory devices. Both applications use transition between the amorphous and crystalline phases that show large optical and electrical-resistivity contrasts. To study crystallization of the amorphous in the applications, it is probably more appropriate to use the one that is reamorphized from the crystalline phase than the one that is as-deposited by a sputtering. This is since the transition is repeated for many times, and there is a paper that indicated as-deposited and reamorphized amorphous-phases are structurally different.[1] Moreover, a reamorphized state may be the mixture of amorphous and crystalline phases.[2-6] Crystallization of the reamorphized state is so far less studied, and one reason may be that preparing a large area of the state (that is often necessary for the evaluation) is rather difficult. We have recently started the study using an optical disc drive tester to make many reamorphized marks in the crystalline area. A fused-silica disc substrate is used (instead of polycarbonate one) to heat the sample directly for (re-)crystallization. An advantage of this approach is that disc properties can also be measured. In this manuscript, crystallization temperature and activation energy of a reamorphized state are tentatively evaluated.

2. EXPERIMENTS

All films were deposited by conventional radio-frequency magnetron sputtering at room temperature, as has been reported elsewhere.[7] Structure of the single layer sample was fused-silica substrate/ $Ge_2Sb_2Te_5$ (thickness: 50 nm), and it of the optical disc sample was fused-silica substrate/ ZnS-SiO_2 (145 nm)/ Ge-N (5 nm)/ $Ge_2Sb_2Te_5$ (20 nm)/ Ge-N (5 nm)/ ZnS-SiO_2 (15 nm)/ Al-Cr (40 nm). One of the two as-deposited optical-disc samples was used to make a reamorphized state for the study. It was first annealed at 200 ˚C for 10 min in air to crystallize $Ge_2Sb_2Te_5$, and then reamorphized marks (mark length: 1 μm) were recorded using an optical disc drive tester (Pulstec Industrial Co., DDU-1000) with a laser wavelength and a numerical aperture of 405 nm and 0.65, respectively. The disc sample was rotated at a speed of 1976 rpm, and it corresponds to the velocity of 6 m/s at the disc radius used for recording. Optical pickup of the tester is located on a stage (Kyodo Denshi System Co., LS90S/OPT) that moves along radial direction of the disc. Distance between each reamorphized-mark trains was 2 μm, and we have prepared 250 trains to make a large area of the reamorphized state. The basic idea of using an optical disc drive tester for large-area lithography can be found in ref. 8. Crystallization properties of the single layer, as-deposited disc, reamorphized disc samples were evaluated by measuring an optical property change during heating. An optical microscope equipped with a white light source (tungsten lamp or xenon lamp) and a multichannel photodetector (Hamamatsu Photonics,

PMA-11) was connected to monitor the reflected (or transmitted) light intensity at a wavelength of 635 nm. Sample heating was performed in air on a heating stage (Linkam Scientific Instruments, LK-1500) at ramp rates (α) of 2, 5, 10 and 20 ˚C/min.

3. RESULTS & DISCUSSION

Figure 1(a) shows the transmitted light intensity change during heating the $Ge_2Sb_2Te_5$ single layer sample with various α conditions. A sharp transmittance drop was observed at around 166 ˚C, and this corresponds to the crystallization of the as-deposited (amorphous) state.[3, 9-13] To obtain the activation energy of this transition, Kissinger's method[14] is used. The crystallization temperature (T_C) was determined from the minimum of the first derivative in each intensity curve. Figure 1(b) shows the result of Kissinger's plots, and the unit of T_C is Kelvin in the figure. From the slope ($-E_a/k_B$, E_a: activation energy, k_B: Boltzmann constant) of the approximation line, we have estimated E_a to be 2.9±0.1 eV. This value is relatively high among previously reported ones in the range of 2-3 eV.[2-5, 9-13]

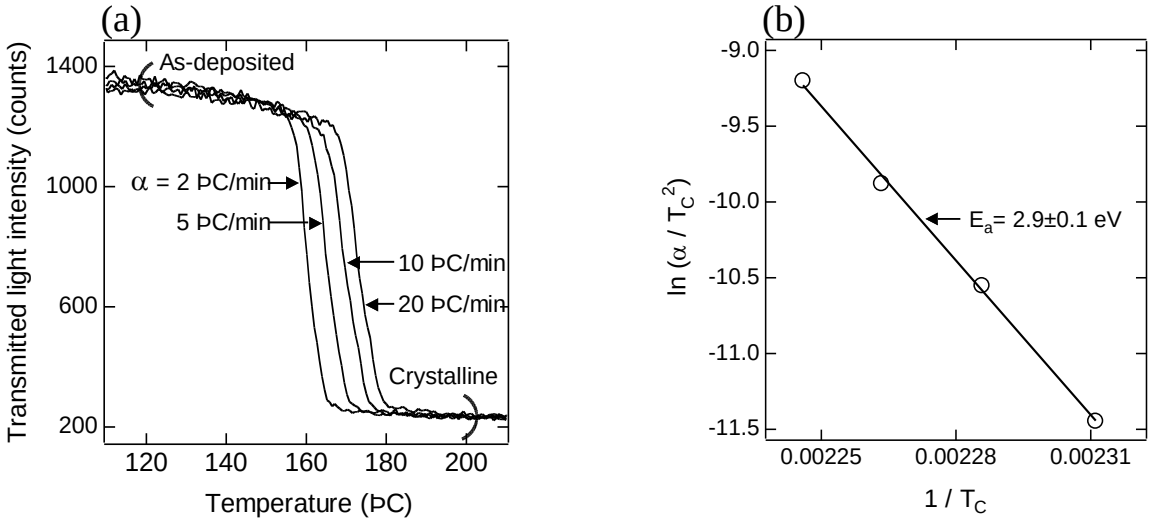

Figure 1 (a) Transmitted light intensity change of the $Ge_2Sb_2Te_5$ single-layer sample at a wavelength of 635 nm. (b) A Kissinger plot of the results in Fig. 1(a) (T_C in Kelvin).

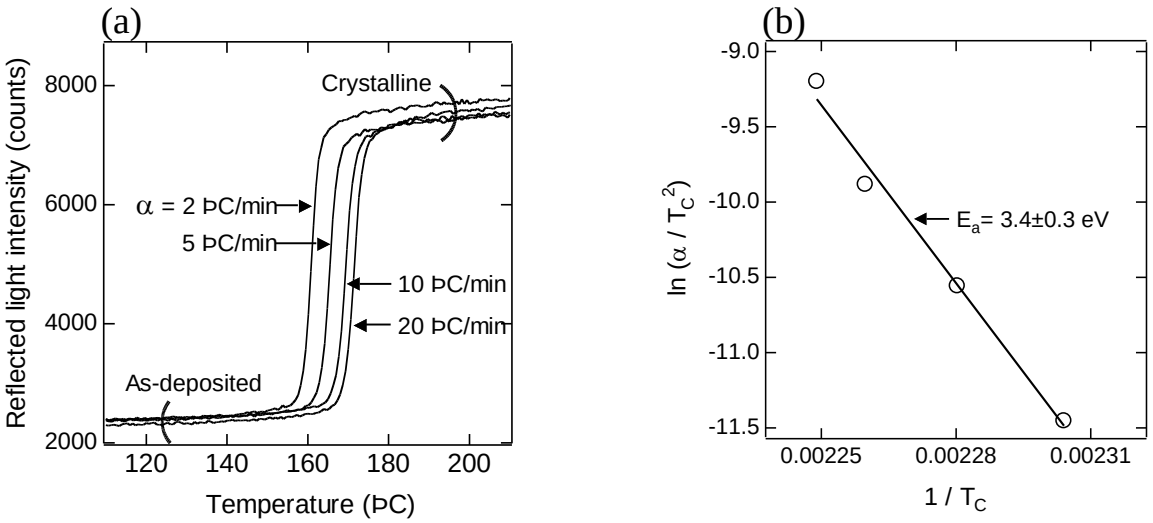

Figure 2 (a) Reflected light intensity change of the optical disc sample (as-deposited) at a wavelength of 635 nm. (b) A Kissinger plot of the results in Fig. 2(a) (T_C in Kelvin).

Figure 2(a) shows the reflected light intensity change during heating the as-deposited disc sample. Since the light intensity increased by the crystallization, the maximum of the first derivative was used to determine T_C. Figure 2(b) shows the result of Kissinger's plots (T_C in Kelvin), and E_a was estimated to be 3.4±0.3 eV. E_a increased by making an optical disc structure, and this is probably since $Ge_2Sb_2Te_5$ layer was capped by dielectric films according to the previous studies.[10, 13]

Figure 3 shows the carrier to noise ratio (CNR) properties of 1-μm-length marks as a function of recording laser power (P_w) for the optical disc sample that is preheated at 200 ˚C (i.e., crystallized). Recording laser beam was focused, and the duty ratio was 50%. It was possible to record at above P_w= 6.0 mW, and the CNR reached 44 dB at P_w= 9.0 mW. Figure 4 shows the CNR properties when repeated the mark recording in Fig. 3 (P_w= 9.0 mW) and erasing by a laser power of 4.0 mW. The results confirmed that the disc is rewritable and a reamorphized state can be formed in the disc sample.

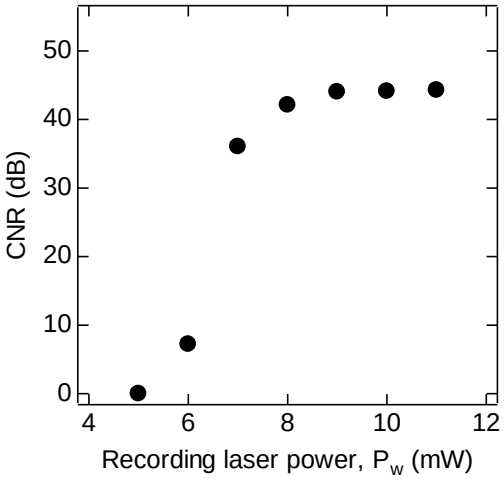

Figure 3 Dependence of the CNR (mark length: 1 μm) on recording laser power of the optical disc sample. $Ge_2Sb_2Te_5$ layer was crystallized before the measurement. Laser wavelength and numerical aperture of the optical disc drive tester was 405 nm and 0.65, respectively.

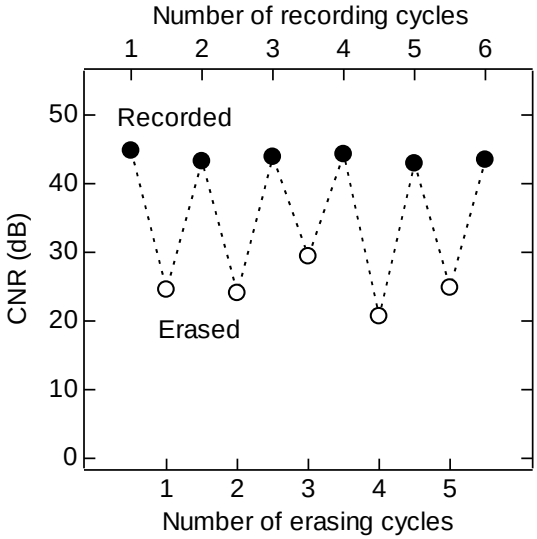

Figure 4 CNR properties when recorded 1-μm reamorphized marks at the laser power of 9.0 mW (duty ratio: 50%) and erased at 4.0 mW. Recording and erasing were repeated without changing the disc-radius position for several times.

Figure 5 shows the laser scanning microscope (reflection) image of the reamorphized mark trains taken at a laser wavelength of 632.8 nm. The marks were recorded at P_w= 9.0 mW (for just one time at each mark train), and the optical pickup is moved along the disc radial direction to record another mark train. The image was observed from the substrate side, and the dark spots correspond to the reamorphized recorded marks. One can confirm that a large area of the reamorphized state is formed as it is designed in the previous section. Upper part of Fig. 6 shows the reflected light intensity change during heating the sample shown in Fig. 5. Lower part of Fig. 6 shows the one of the same disc sample but of the disc area where reamorphized marks were not recorded. The rate α was both 20 ˚C/min. For the recorded, a small intensity increase was observed at around 138 ˚C. By comparing the results in Fig. 6, its origin can be attributed to the reamorphized marks. The intensity increase is probably due to its (re-)crystallization since the temperature was also close to the previously reported T_C that is in the range of 140-170 ˚C.[3, 9-13]

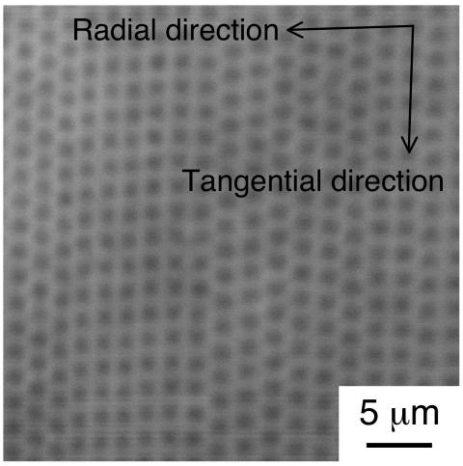

Figure 5 Laser scanning microscope (reflection) image of the 1-μm reamorphized mark trains (wavelength: 632.8 nm). The image was converted to a gray scale.

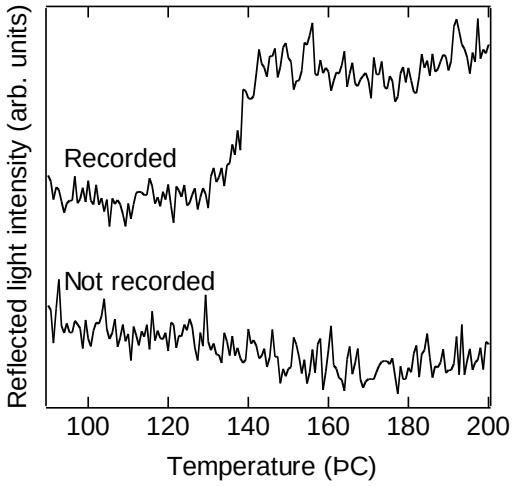

Figure 6 Reflected light intensity change of the crystallized optical disc sample where the reamorphized marks are recorded (Fig. 5) and not recorded. The intensity was observed at a wavelength of 635 nm, and the temperature ramp rate (α) was 20 ˚C/min.

Figure 7(a) shows the dependence of α when heating the reamorphized disc sample. The intensity curve for α= 20 ˚C/min is a duplicate of the one shown in upper part of Fig. 6. Since the intensity change due to crystallization was small and the intensity variation at the starting temperature was relatively large among the heating experiments, the starting intensities were normalized to 100 in the figure. It should be noted that even when the light intensity was measured at a wavelength of 405 nm that is used in the disc property experiment (in Figs. 3 and 4), rate of the intensity increase was still about 4%. Figure 7(b) shows the result of Kissinger's plots (T_C in Kelvin). Since the original intensity curves in Fig. 7(a) were rather noisy, it was not easy to determine T_C simply from their first derivative. We further fitted the derivative with a Lorentzian curve to determine the maximum and thus T_C in the figure. E_a was estimated to be 2.3 eV, and its error was less than ±0.1 eV.

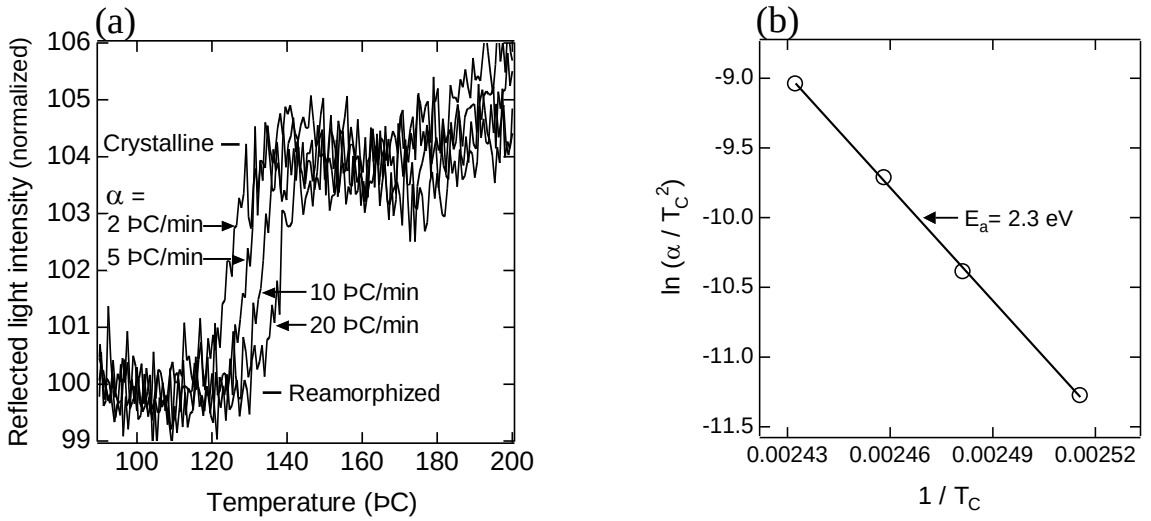

Figure 7 (a) Reflected light intensity change of the optical disc sample (reamorphized) at a wavelength of 635 nm. The starting intensities were normalized to 100. (b) A Kissinger plot of the results in Fig. 7(a) (T_C in Kelvin).

Crystallization properties of $Ge_2Sb_2Te_5$ are also dependent on its surrounding medium,[10, 13] and we probably need to make the ratio of reamorphized area in Fig. 5 to ~100% for a direct comparison of the two amorphous (i.e., as-deposited and reamorphized) states. However, a reamorphized part is often formed inside the crystalline medium when used in the applications, and we believe that evaluating such a coexisting condition (e.g., an optical disc in Fig. 5) is rather important. A comparison of the results in Figs. 2 and 7 indicated that both T_C and E_a decreased in the reamorphized sample by about 35 ˚C and 1.1 eV, respectively. It should be noted that E_a of the reamorphized sample in Fig. 7 was also within the range of the previously reported ones.[2-5, 9-13] Contrary to the large reflected light intensity change for the as-deposited state in Fig. 2(a), the one for the reamorphized state in Fig. 7(a) was considerably small. This is partly since the reamorphized area was just quarter of the total area (as shown in Fig. 5), but we still can expect from Fig. 2(a) that the starting intensity (normalized to 100) will change to roughly 150 by the recrystallization in Fig. 7(a). A lack of the sufficient intensity change may suggest that the reamorphized state prepared was not just formed by the amorphous phase, but a mixture of the crystalline and amorphous phases. We are not sure if the amorphous phase formed is identical to the one of as-deposited or not[1] at the moment. Previous studies have indicated that the reamorphized state contains crystalline nuclei and it lowers E_a by 0.2-0.3 eV.[3-6] Decrease of E_a in this study may support the assumption of mixing, and a further structural study is needed for its direct evidence. In addition, we need to take an effect of stress release at the $Ge_2Sb_2Te_5$ layer (by melting) into account since it is also expected to decrease E_a.[10, 13]

For preparing the reamorphized marks, we optimized the P_w condition in Fig. 3 but not the duty ratio condition. It is known that the shape and structural properties of the reamorphized mark are also dependent on the duty ratio and number of the recording laser pulses. Modifying the recording conditions will presumably bring different T_C and E_a, and correlating them with the structural properties is also an important issue for better understanding of the recrystallization.

4. CONCLUSION

We have prepared a rewritable optical disc (phase change layer: $Ge_2Sb_2Te_5$) on fused silica substrate to study the crystallization properties of both as-deposited and reamorphized states. A large area with 1-μm reamorphized marks was successfully made and is heated to recrystallize. Crystallization temperature and activation energy were about 131 ˚C and 2.3 eV, respectively, for the reamorphized sample, and they both decreased from the ones of the as-deposited. A direct comparison of the two states confirmed that the crystallization properties are dependent on the reamorphized mark condition and on the surrounding crystalline medium. The results also suggest that it is more appropriate to use a device-like structure with a reamorphized state to evaluate the crystallization of the phase change material when used in the applications.

REFERENCES

1. A.V. Kolobov, P. Fons, A.I. Frenkel, A.L. Ankudinov, J. Tominaga and T. Uruga: “Understanding the phase-change mechanism of rewritable optical media”, Nature Materials **3** (2004) 703.

2. C. Trappe, B. Béchevet, S. Facsko, and H. Kurz: “Real time measurements of phase change dynamics”, Jpn. J. Appl. Phys. **37** (1998) 2114.

3. J. Park, M.R. Kim, W.S. Choi, H. Seo, and C. Yeon: “Characterization of amorphous phases of $Ge_2Sb_2Te_5$ phase-change optical recording material on their crystallization behavior”, Jpn. J. Appl. Phys. **38** (1999) 4775.

4. V. Weidenhof, I. Friedrich, S. Ziegler, and M. Wuttig: “Laser induced crystallization of amorphous $Ge_2Sb_2Te_5$ films”, J. Appl. Phys. **89** (2001) 3168.

5. S. Privitera, C. Bongiorno, E. Rimini, and R. Zonca: “Crystal nucleation and growth processes in $Ge_2Sb_2Te_5$”, Appl. Phys. Lett. **84** (2004) 4448.

6. P.R. Khulbe, E.M. Wright, and M. Mansuripur: “Crystallization behavior of as-deposited, melt quenched, and primed amorphous states of $Ge_2Sb_{2.3}Te_5$ films”, J. Appl. Phys. **88** (2000) 3926.

7. T. Shima, Y. Yamakawa, and J. Tominaga: “Readout durability improvement of super-resolution near-field structure discs with PtO_x-SiO_2 recording and GeN_y interfacial layers”, Jpn. J. Appl. Phys. **46** (2007) L135.

8. K. Kurihara, Y. Yamakawa, T. Nakano, and J. Tominaga: “High-speed optical nanofabrication by platinum oxide nano-explosion”, J. Opt. A **8** (2006) S139.

9. N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira, and M. Takao: “Rapid-phase transitions of GeTe-Sb_2Te_3 pseudobinary amorphous thin films for an optical disk memory”, J. Appl. Phys. **69** (1991) 2849.

10. I. Friedrich, V. Weidenhof, W. Njoroge, P. Franz, and M. Wuttig: “Structural transformations of $Ge_2Sb_2Te_5$ films studied by electrical resistance measurements”, J. Appl. Phys. **87** (2000) 4130.

11. E. Morales-Sánchez, E.F. Prokhorov, J. González-Hernández, and A. Mendoza-Galván: “Structural, electric and kinetic parameters of ternary alloys of GeSbTe”, Thin Solid Films **471** (2005) 243.

12. Y. Kim, S.A. Park, J.H. Baeck, M.K. Noh, K. Jeong, M.-H. Cho, H.M. Park, M.K. Lee, E.J. Jeong, D.-H. Ko, and H.J. Shin: “Phase separation of a $Ge_2Sb_2Te_5$ alloy in the transition from an amorphous structure to crystalline structures”, J. Vac. Sci. Technol. A **24** (2006) 929.

13. K. Nishiuchi, N. Yamada, K. Kawahara, and R. Kojima: “Effect of dielectric material films on crystallization characteristics of $Ge_2Sb_2Te_5$ phase-change memory film”, Jpn. J. Appl. Phys. **46** (2007) 7421.

14. H.E. Kissinger: “Reaction kinetics in differential thermal analysis”, Anal. Chem. **29** (1957) 1702.

Biographies

Takayuki Shima received the B.E., M.E., and Dr. Eng. from Chiba University, Japan in 1992, 1994, and 1997, respectively. He was an Industrial Technology Researcher of New Energy and Industrial Technology Development Organization (NEDO), Japan during 1997-2000. He was a Domestic Research Fellow of Japan Science and Technology Corporation (JST) and Japan Society for the Promotion of Science (JSPS) during 2001-2003. He joined National Institute of Advanced Industrial Science and Technology, Japan in 2003. He is a member of Japan Society of Applied Physics (JSAP), Materials Research Society (MRS), and The Institute of Image Information and Television Engineers. His current research interests include development of materials for high-capacity optical data storage media.