Effect of Interface Layers on Phase-change Recording Material Analyzed by HX-PES Method

Phase-change storage technology has been developed for rewritable optical media and recently for the nonvolatile semiconductor memory. The history of the technology is long and began with the discovery of reversible electrical switching in a chalcogenide compound by Ovshinsky [1]. Kolobov *et al*. recently proposed a novel phase-change model for GeSbTe (GeTe-Sb_2Te_3: GST) based on an X-ray absorption fine structure (XAFS) study [2]. On the other hand, research for industrial application is more advanced than fundamental research, i.e., the understanding of the fast phase-change mechanism. Two main types of materials have already been used practically for phase-change recording media. One is the pseudobinary compound GeSbTe (GST). The other is a eutectic alloy, which is typically an SbTe alloy that has been known for a long time to be a compound semiconductor having a narrow band gap. On the basis of various evidence, it is also known that the crystallization mode of a pseudobinary phase-change material is different from that of a eutectic alloy phase-change material. In addition, the interface layer, which is a very thin dielectric layer located immediately above the recording layer, is important for the practical use of phase-change media. The effect of the interface layer material on the phase-change recording material is only understood phenomenologically. The development of high-speed phase-change material is crucial for the high-speed operation of the media, because the erase process of rewritable media corresponds to the crystallization process. In other words, it is necessary for both the development of high-speed phase-change materials and the understanding of the effect of the interface layer on the recording layer from a microscopic viewpoint, including the characterization of the chemical and electronic states of the phase-change recording material in actual media. However, the analysis of the actual media presents various challenges. For example, the recording layer is buried beneath other films. The thickness of a protection layer is over 30 nm. On the other hand, the detection depth of conventional X-ray photoelectron spectroscopy (XPS) is below a few nm [3]. An etching process is required to detect the signal from the recording layer using conventional laboratory XPS, because conventional XPS is only sensitive to the surface. The etching process alters the interface between the two films. Thus, it is difficult to detect the detailed chemical state of samples having a structure used in actual media. However, hard-X-ray photoelectron spectroscopy (HX-PES), which has a large probing depth, has been developed [4].

The effect of the interface layer on the pseudobinary material and the eutectic alloy used as phase-change recording materials was investigated at room temperature for the first time by HX-PES to clarify the high-speed phase-change recording mechanism. The HX-PES experiments were performed at beamline **BL47XU**. GeBiTe (GeTe-Bi_2Te_3: GBT) and SbTe alloys were adopted as the pseudobinary compound and eutectic alloy, respectively. GBT is used for high-speed rewritable HD DVD media, as shown in Fig. 1(a). Samples

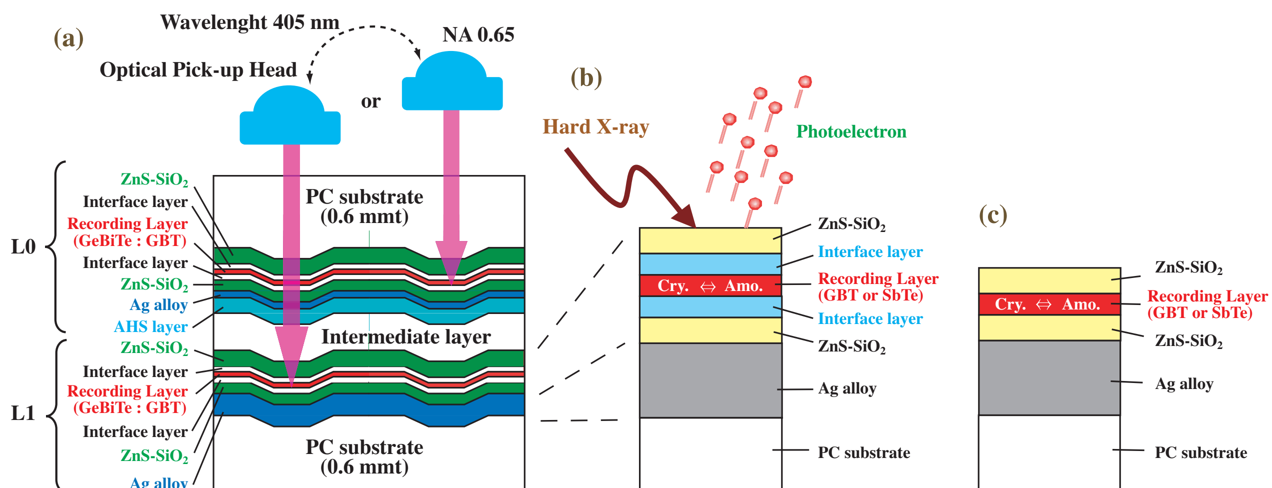

Fig. 1. **(a)** Cross-sectional view of the dual-layer rewritable HD DVD media and the sample used for HX-PES: **(b)** with interface layers and **(c)** without interface layers.

having a structure used in actual media were prepared with interface layers on both sides of the recording material (Fig. 1(b)) and without interface layers (Fig. 1(c)) for comparison. We used GBT and SbTe films with a thickness of 5 nm, which is similar to that used in actual media. The interface layers were oxide-based and nitride-based compounds with a high crystallization acceleration function. We did not include Ge, Sb, Te, or Bi in the interface layers. We also used other interface-layer materials that had similar crystallization acceleration functions. However, the obtained results from HX-PES were similar for all samples having interface layers. The film stack was deposited on a 0.6-mm-thick PC substrate using manufacturing-scale sputtering equipment (OCTAVA-II: Shibaura Mechatronics). Along with a sample having an as-deposited amorphous recording film, a sample with a crystalline recording film was prepared. The recording film was crystallized using the same initialization equipment as that used for the initialization of rewritable HD DVDs.

Figure 2 shows photoemission spectra for the valence band of GBT with and without interface layers obtained by HX-PES. They are almost equivalent to the density of states (DOS) for the valence band of GBT. The DOS for the amorphous state without interface layers is smaller than that of the crystalline GBT. The band-edge energy of the amorphous state without interface layers is lower than that of the crystalline state by about 0.5 eV. On the other hand, the DOS of the valence band and the band-edge energy of the amorphous GBT with interface layers are almost same as those of the crystalline state. This result may lead to almost the same carrier density required for the electrical conduction of the crystalline and amorphous states, which is completely unexpected and thus very interesting because the atomic arrangements should differ from each other. This is confirmed by investigating actual media nondestructively by EXAFS analysis at beamline **BL16B2** [5]. We speculate that this effect is a factor required for high-speed crystallization.

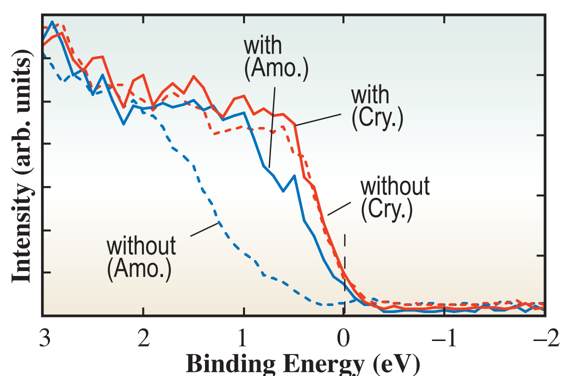

Fig. 2. Photoemission spectra for valence band of the GBT film without and with interface layers.

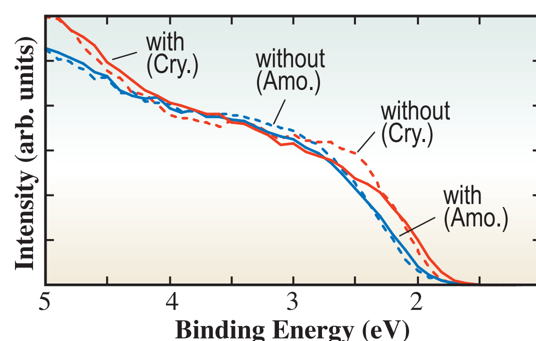

Fig. 3. Photoemission spectra for valence band of the SbTe film without and with interface layers.

The photoemission spectra from the valence band of the crystalline SbTe films showed very little difference from those of the amorphous SbTe films regardless of whether or not they were in contact with the interface layers (Fig. 3). This behavior is similar to the results for the pseudobinary recording films with the interface layers, but is in contrast with the pseudobinary recording films without interface layers. These results suggest a difference in the crystallization mode between the pseudobinary alloy and the eutectic compound.

These findings are useful for understanding the phase-change mechanism of optical recording media. Also, they can be applied for the research of semiconductor devices such as phase-change random access memories (PRAMs).

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References

[1] S. Ovshinsky: Phys. Rev. Lett. **21** (1968) 1450.
[2] A.V. Kolobov *et al.*: Nature Materials **3** (2004) 703.
[3] T. Nakai, M. Yoshiki and N. Ohmachi: Jpn. J. Appl. Phys. **46** (2007) 3968.
[4] For example, K. Kobayashi: BUTSURI **60** (2005) 624 [in Japanese].
[5] *T. Nakai, M. Yoshiki and Y. Satoh: Proc. SPIE* ***6620*** *(2007) 66202c-1.*