Microstructure and recording mechanism of Ge/Au bilayer media for write-once optical disc

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The recording mechanism of Ge/Au bilayer and its dynamic tests for write-once blue laser high density DVD (HD DVD) are investigated. It is found that Ge_2Au_3 phase is nucleated between amorphous Ge and crystalline Au layer after room temperature deposition. Crystallization of Ge/Au interface layer at 170–190 °C is induced by the nucleated Ge_2Au_3 sites at the interface, the bilayer structure is further heated to 200–450 °C. After heating above 320 °C, crystallized Ge are segregated at the grain boundary. The dynamic test results show that this Ge/Au bilayer films can be applied to 1× –2× HD DVD-R.
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Organic materials are commonly used as the recording media of write-once optical disc. However, some issues needed to be solved in the blue ray condition, such as low optical absorption, bad adhesion in narrow track pitch with spin coating process, and the toxicity. As a result, the environmentally friendly inorganic materials are developed to replace the organic media in recent years. Amorphous silicon (*a*-Si) was a promising candidate due to its low cost, but its high crystallization temperature (700 °C) was the main limitation for inorganic write-once media. Later, metal induced crystallized Si with low crystallization temperature were proposed,[1–5] and the studies on the mechanism of metastable phase formation at low temperature and *c*-Si or metal segregation at high temperature were investigated. The *a*-Si/Cu (semiconductor/metal) bilayer recording media for Blu-ray disc (BD) write-once disc was proposed in 2003.[6] After that, various bilayer recording media were reported subsequently.[7–9] However, none of these proposals discussed the mechanism of microstructure change at interface layer. On the other hand, germanium (Ge) exhibit similar physical and chemical behaviors as Si, and the crystallization temperature of Ge was only 400–420 °C,[10] which is much lower than that of *a*-Si. According to the phase diagram of Ge–Au,[11] the eutectic temperature of GeAu was 361 °C which was a suitable character for optical recording media. In this letter, we report the microstructure and recording mechanism of Ge/Au bilayers. The microstructure changes before and after heating are discussed in accordance with the nanoscale transmission electron microscopy (TEM) cross-sectional image of Ge/Au bilayer.

The layer structure of 1× –2× high density (HD) DVD write-once disk with Ge/Au bilayer recording films is shown in Fig. 1. The lower dielectric layer, Ge/Au bilayer, upper dielectric layer, and Ag reflective layer were deposited on 0.6 mm thick polycarbonate (PC) substrates and nature oxidized (110) silicon substrates by commercial sputtering system (Modulus, Singulus). The sample with PC disc substrate was bonded with a dummy substrate of 0.6 mm thick. Its partial response signal to noise ratio (PRSNR) and simulation bit error rate (SbER) were evaluated by using a dynamic tester (ODU1000, Pulstec), the test conditions are shown in Table I. The sample with Si substrate was investigated by thermal analyzer. The phase transition temperature (T_c) and the relationship between reflectivity and temperature were measured. These samples were heated in vacuum oven (10^{-5} torr) for 30 min and then quenched in ice water. Microstructure images and electron diffraction patterns of the as-deposited and annealed samples were taken by field emis-

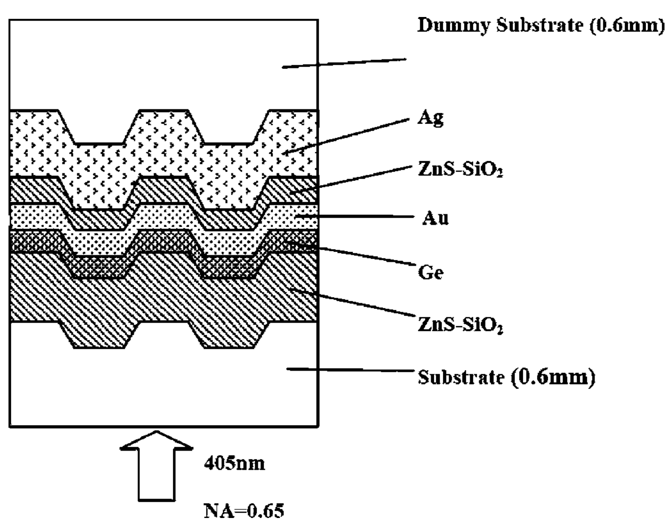

FIG. 1. Layer structure of the Ge/Au write-once optical disk.

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TABLE I. Dynamic recording conditions.

User capacity (Giga byte)	15	
Thickness of substrate (mm)	0.6	
Wavelength (nm)	405	
Numerical aperture	0.65	
Modulation code	ETM, RLL (1,10)	
Track pitch (μm)	0.4	
Channel clock frequency (MHz)	64.8	
Linear velocity (m/s)	6.6	13.2
User bit rate (Mbyte/s)	36.55	73.1

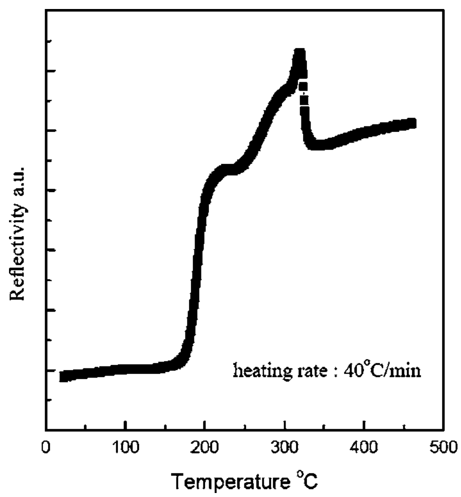

FIG. 2. Relationship between the reflectivity and temperature.

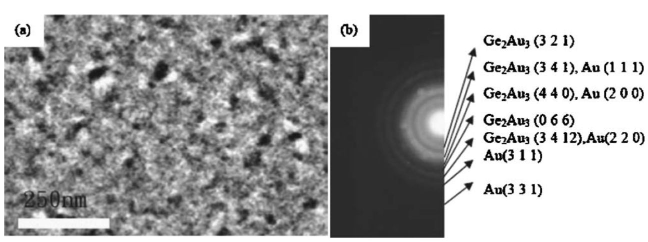

FIG. 3. (a) TEM bright field image and (b) electron diffraction pattern of the as-deposited Ge/Au bilayers.

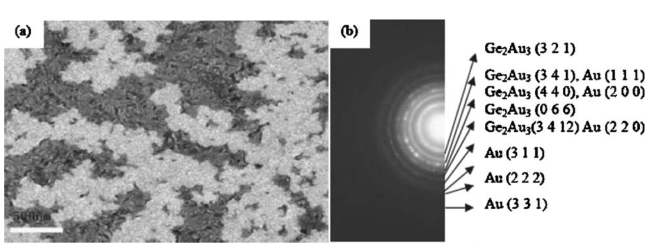

FIG. 4. (a) TEM bright field image and (b) electron diffraction pattern of the GeAu bilayers after 220 °C, 30 min annealing.

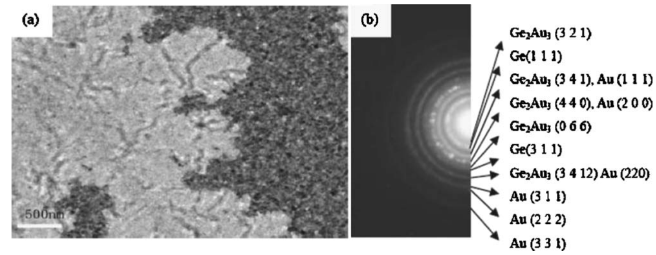

FIG. 5. (a) TEM bright field image and (b) electron diffraction pattern of the GeAu bilayers after 320 °C, 30 min annealing.

sion gun transmission electron microscope (FEGTEM) and compared. The samples for TEM plane view were sputtered on a 3 mm diameter copper mesh which fits the TEM holder. The phase change temperature was evaluated by measuring the reflectivity change as a function of increasing temperature by homemade thermal analyzer.

Figure 2 shows reflectivity of Ge/Au bilayer with temperature. It is evident that increasing the temperature to 170–190 °C, the reflectivity has a sharp rising step. As the temperature is further increased from 200 to 310 °C, the reflectivity shows an unstable rising and then drops quickly between 310 and 320 °C and becomes almost constant until 460 °C. These changes in reflectivity are related to the microstructural changes and the variation of composition. According to these results, we chose the annealing temperatures of 220 and 320 °C to examine the microstructures of Ge/Au bilayer films.

Figures 3(a) and 3(b) shows the TEM bright field images and the selected area diffraction (SAD) patterns of the as-deposited Ge/Au bilayer, respectively. Figure 3(a) indicates that the as-deposited Ge/Au bilayer is in crystalline state; crystalline phases of Ge_2Au_3 and Au are identified in Fig. 3(b). When this Ge/Au bilayer is heated to 220 °C, formation of dendrites is found on the film surface, as shown in Fig. 4(a), and diffraction patterns of Ge_2Au_3 and Au phases, as shown in Fig. 4(b), are similar with as-deposited bilayers [Fig. 3(b)]. When the temperature is increased to 320 °C, it is found that the dendrites are mixed, as shown in Fig. 5(a), and the SAD images, as shown in Fig. 5(b), suggests that the crystalline Ge phase appeared.

Figure 6 shows the cross-sectional view of as-deposited Ge/Au bilayer. It is evident that GeAu interface layer of

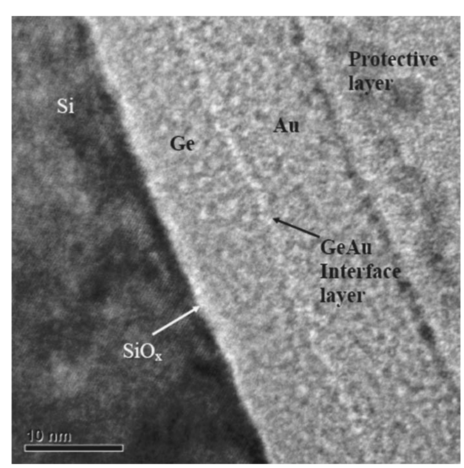

FIG. 6. Cross-sectional view of as-deposited $ZnS-SiO_x$/Ge(8 nm)/Au(8 nm)/Si substrate.

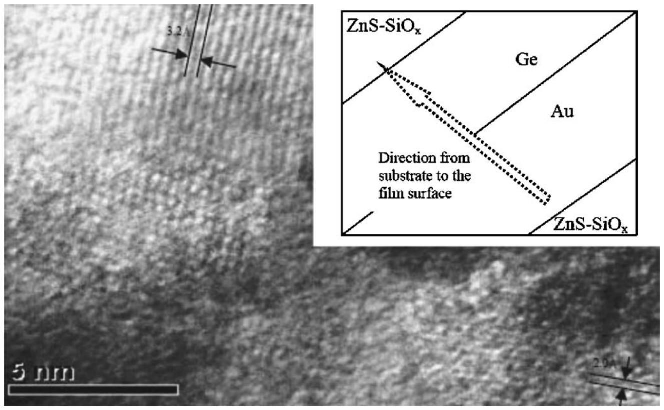

FIG. 7. Cross-sectional view of ZnS–SiO$_x$/Ge(8 nm)/Au(8 nm)/ZnS–SO$_x$/Si substrate after annealing at 220 °C for 30 min. The arrow mark shows the direction from the substrate to the film surface.

1 nm thickness is formed between amorphous Ge and crystalline Au layer. Comparing with the SAD of the as-deposited films, besides the Au grains, the GeAu crystal phase also appeared [see Fig. 3(b)]. These are the original nucleation sites during the sputtering process. Figure 7 shows the cross-sectional image of the Ge/Au bilayer after annealing at 220 °C temperature for 30 min. On the upper-left side of the figure, the *d* spacing of the grain is 3.20 Å. Comparing with the JCPDS card, the *d* spacing of Ge_2Au_3 (3 2 1) is 3.1952 Å. Therefore, Ge_2Au_3 (3 2 1) is the most possible orientation of the grains. On the other hand, the *d* spacing of the lower-right side of the image was identified as 2.02 Å, and was comparable with the *d* spacing of Ge_2Au_3 (4 4 0) and Au (2 0 0), i.e., 2.0317 and 2.0398 Å, respectively. These are the most possible orientation of the grains. Consequently, interdiffusion of Au and Ge atoms begins at interface layer, the metastable phase of Ge_2Au_3 (3 2 1) is formed due to the *d* spacing of Ge_2Au_3 (3 2 1) (d=3.1952 Å) is about equivalent to the closed packed plane of Ge (1 1 1) (d=3.2663 Å). The formation of Ge_2Au_3 leads to the first step of reflectivity change in Fig. 2. When the annealing temperature is further increased to 320 °C, Ge segregation leads to the drop of reflectivity at 310–320 °C. Figure 8 shows the dynamic test result that the values of PRSNR and SbER change with writing powers. The suggested PRSNR and SbER need to be larger than 15 dB and lower than 5 $\times 10^{-5}$, respectively, for HD DVD.[12] As we can see in the Fig. 8, suitable power for 1× recording speed is 7.8–8.2 mW and 8.8–9.1 mW for 2× recording speed. And the contrast was between 70% and 78% at wavelength of 405 nm.

In summary, we have investigated the recording mechanism of Ge/Au bilayer for HD DVD write-once recording media. Two steps of phase change are obtained. The as-deposited Ge/Au bilayer has a crystalline 1 nm thick Ge_2Au_3 interlayer and a crystalline Au film. The Ge_2Au_3 crystallites initially formed at the interface act as nucleation sites during recording. During heating at 170–190 °C, Ge_2Au_3 grains grow and the Ge_2Au_3 (3 2 1) phase are formed due to the similar *d* spacing between the close packed plane of Ge (1 1 1) and Ge_2Au_3 (3 2 1). The formation of Ge (1 1 1) grains is found after heating at

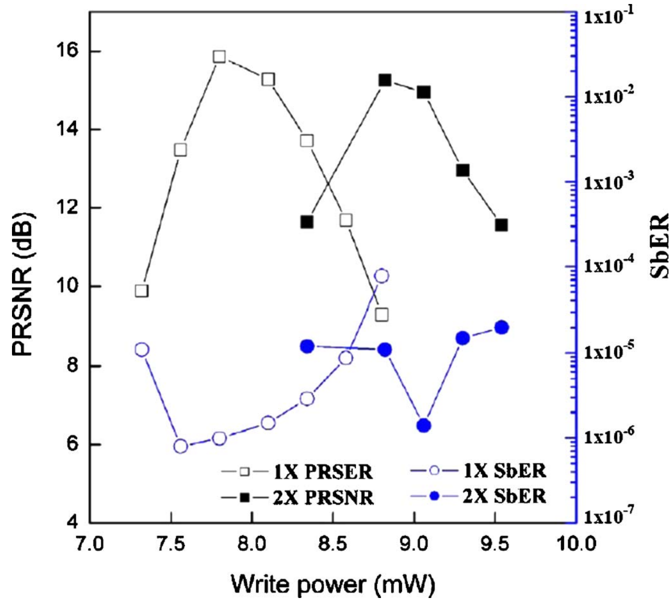

FIG. 8. (Color online) PRSNR and SbER as a function of the peak power at the 1× and 2× recording speeds.

310–320 °C. As a result, the film has Ge, Ge_2Au_3, and Au crystalline phases after recording. Metal induced crystallization mechanism is confirmed by the FEGTEM cross-sectional view and thermal analysis. PRSNR and SbER values of 16.0 dB with 9.9×10^{-7} and 15.2 dB with 1.4×10^{-6} suggest that the Ge/Au bilayer is suitable for the recording speed of 1× and 2× HD DVD, respectively.

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[1] S. W. Russell, Jian Li, and J. W. Mayer, J. Appl. Phys. **70**, 5153 (1991).
[2] Bo Bian, Jian Yie, Boquan Li, and Ziqin Wu, J. Appl. Phys. **73**, 7402 (1991).
[3] Jae-Bok Lee, Chan-Jae Lee, and Duck-Kyun Cho, Jpn. J. Appl. Phys., Part 1 **40**, 6177 (2001).
[4] Bo Bian, Jian Yie, Boquan Li, and Ziqin Wu, J. Appl. Phys. **73**, 1 (1993).
[5] L. Hultman, A. Robertsson, H. T. G. Hentzell, I. Engstrom, and P. A. Psaras, J. Appl. Phys. **62**, 1 (1987).
[6] Hiroyasu Inoue, Kouji Mishima, Masaki Aoshima, Hideki Hirata, Tatsuya Kato, and Hajime Utsunomiya, Jpn. J. Appl. Phys., Part 1 **42**, 1059 (2003).
[7] Yung-Chiun Her, Chih-Wei Chen, and Chun-Lin Wu, J. Appl. Phys. **99**, 113512 (2006).
[8] Jung-Po Chen, Chih-Yuan Wu, Po-Fu Yen, Tzuan-Ren Jeng, and Der-Ray Huang, Proceedings of the Asia-Pacific Data Storage Conference, 2006 (unpublished), p. 136.
[9] Shih-Hsien Ma, Chin-Yen Yeh, Huang-Chang Chen, Sheng-Huan Liu, and Donyau Chaing, Proceedings of the Asia-Pacific Data Storage Conference, 2006 (unpublished), p. 140.
[10] Fumiya Oki, Yoshio Ogawa, and Yoshibuni Fujiki, Jpn. J. Appl. Phys. **8**, 1056 (1969).
[11] *Binary Alloys Phase Diagrams*, edited by B. Thaddeus, J. L. Murray, L. H. Bennett, and H. Baker, 2nd ed. (American Society for Metals, Metals Park, OH, 1986), Vol. 1, p. 373.
[12] Ming Chia Li, Andrew Li, Chien-Liang Huang, Ching-Yu Hsien, Chi-Min Lin, WenYih Liao, Tzuan-Ren Jeng, Proceedings of the International Symposium on Optical Memory, 2006 (unpublished), Paper No. Th-I-10.