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Research Article

Microstructures and Recording Mechanism of Mo/Si Bilayer Applied for Write-Once Blue Laser Optical Recording

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Mo/Si bilayer thin films were grown by magnetron sputtering and applied to write-once blu-ray disc (BD-R). The microstructures and optical storage properties of Mo/Si bilayer were investigated. From the temperature dependence of reflectivity measurement, it was revealed that a phase change occurred in the range of 255–425°C. Transmission electron microscopy analysis showed that the as-deposited film possessed Mo polycrystalline phase. The hexagonal $MoSi_2$ and cubic Mo_3Si phases appeared after annealing at 300 and 450°C, respectively. By measuring the optical reflectivity at a wavelength of 405 nm, the optical contrast of Mo/Si bilayer between as-deposited and 450°C-annealed states was evaluated to 25.8%. The optimum jitter value of 6.8% was obtained at 10.65 mW for 4× recording speed. The dynamic tests show that the Mo/Si bilayer has high potential in BD-R applications.

1. Introduction

For write-once blu-ray disc (BD-R), amorphous silicon (a-Si) was used as a recording layer due to its advantages of low cost and easy fabrication process. However, the high crystallization temperature of 700°C for a-Si is a serious shortcoming, leading to a high writing power in the recording characteristics. It is well known that metal induced crystallization (MIC) can be applied to decrease the crystallization temperature of a-Si by introducing various metals [1–5]. Therefore, several metal/a-Si bilayer structures such as Cu/Si [6], Al/Si [7], Ni/Si [8], and Cu-Al/Si [9] have been proposed as the recording films of BD-R.

It has been reported that the crystallization temperature of a-Si in Mo/Si multilayer films was ranging from 200 to 400°C [10], indicating that the Mo/Si based films could be suitable for BD-R. Actually, Mo/Si structured mirrors have been widely studied for applications in extreme ultraviolet lithography because of their high normal incidence reflectance [11–15]. Nevertheless, it has not been found that the Mo/Si based thin films were applied to optical recording media. In this study, we presented the Mo (7 nm)/Si (7 nm) bilayer as the recording film of BD-R. The crystallization temperature, microstructures, and recording characteristics of this bilayer were analyzed and discussed.

2. Experimental Procedure

The Mo (7 nm)/Si (7 nm) bilayer was grown on nature oxidized Si wafers and polycarbonate (PC) substrates at room temperature by magnetron sputtering using the Mo and Si targets. In order to apply the Mo/Si bilayer to write-once optical recording media, the multilayer of Ag reflective layer (95 nm)/ZnS-SiO_2 (35 nm)/Mo (7 nm)/Si (7 nm)/ZnS-SiO_2 (24 nm) was fabricated on 1.1 mm-thick PC substrate which has a track pitch of 0.32 μm. Afterwards, a PC transparent cover layer with 0.1 mm thickness was covered on the top of these layers by spin-coating. The crystallization temperature of as-deposited specimen was measured by a home-made reflectivity-temperature analyzer. The microstructures and crystal orientations of the samples before and after annealing

Table 1: Dynamic test conditions.

User capacity	25 GB
Thickness of substrate	1.1 mm
Wavelength	405 nm
Numerical aperture (N.A.)	0.85
Modulation code	(1, 7) RLL
Track pitch	0.32 μm
Linear velocity	4.92 m/s (1×), 19.68 m/s (4×)
Recording format	On groove

were characterized by transmission electron microscopy (TEM). Relationship between reflectivity and wavelength was measured by means of a UV-VIS-NIR spectrophotometer (Perkin-Elmer Lambda 900). To study the diffusion characteristic of Mo/Si bilayer, the element concentration depth profiles of the as-deposited and annealed samples were analyzed using Auger electron spectrometer (AES). The recording characteristics of the discs were evaluated by a dynamic tester (ODU-1000, PULSTEC), and the testing conditions were shown in Table 1. The wavelength of the laser beam is 405 nm and the numerical aperture (N.A.) of the objective lens is 0.85. The modulation code is (1, 7) RLL. The linear velocities of 1× and 4× recording speeds are 4.92 and 19.68 m/s, respectively.

3. Results and Discussion

Figure 1 exhibits the reflectivity changes as a function of temperature for the Mo/Si bilayer at a heating rate of 20°C/min. The measured temperature was increased from room temperature to 550°C using a resistive heater. It can be found that the reflectivity has a decrease as the temperature heated from 255 to 425°C. According to previous research, as the films undergo a structural transition, it could lead to the change of optical reflectivity [16]. Therefore, we choose the temperatures of 300 and 450°C to perform the annealing experiments and examine the microstructures of these films.

The TEM bright field image and electron diffraction pattern of the as-deposited Mo/Si bilayer are shown in Figure 2. It reveals that the as-deposited film has Mo polycrystalline phase with the grain size of 5 nm, and the diffraction pattern rings are identified to Mo (110), Mo (200), and Mo (211). After annealing at 300°C for 15 min, the grain size of Mo/Si bilayer was enlarged and the hexagonal $MoSi_2$ phase (h-$MoSi_2$) appeared, as shown in Figure 3. It is noted that the formation of Mo silicide in Mo/Si multilayers is attributed to the interdiffusion of Mo and Si atoms [17]. As the annealing temperature was increased to 450°C for 15 min, we found that the grains can be divided into two parts, that is, the smaller grains (red circle) and larger grains with the size about 100–300 nm, as shown in Figure 4(a). The analysis of electron diffraction pattern also indicated that two phases existed in the film, one was h-$MoSi_2$ and the other was determined to be Mo_3Si phase. The h-$MoSi_2$ phase with continuous and clear diffraction rings were contributed from the small grains. On the other hand, the discontinuous rings

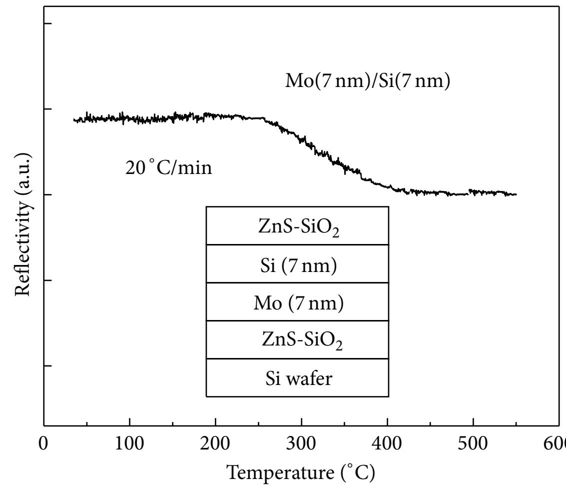

Figure 1: Relationship between the reflectivity and temperature of the as-deposited Mo/Si bilayer at a heating rate of 20°C/min.

corresponding to Mo_3Si phase could result from the large grains. Mo_3Si phase has the cubic A15 structure such as β-W and Cr_3Si [18]. This structure consists of Si atoms occupied the body centered cubic (bcc) positions in the unit cell and the Mo atoms form three orthogonal chains located in the [100] directions on the cube faces. To check the structure of the large grains precisely, the grain which was marked by red arrow was selected to examine by selected area electron diffraction (SAED) pattern. It shows that the large grain has Mo_3Si phase with [011] zone axis, as shown in Figure 4(b). Some reports indicated that the crystallization Si formed in the Mo/Si multilayer after annealing. However, there is no formation of crystallization Si in our results. Murarka et al. [19] have shown the relationship between Mo/Si atomic ratio and the formation in Mo-Si thin films. While the Mo/Si atomic ratio in the film was greater than 0.5, it revealed that only the Mo silicide including $MoSi_2$, Mo_3Si, and Mo_3Si_2 can be observed after annealing. On the contrary, both the Mo silicide and Si crystallization appeared after annealing as the Mo/Si atomic ratio was less than 0.5. Consequently, the atomic ratio of Mo to Si in the interdiffused region of our annealed Mo/Si bilayer was probably greater than 0.5. As we calculated, the number of Mo atoms in the Mo/Si bilayer with the thickness ratio of 1 : 1 was about ten times larger than that of Si atoms. As a result, no crystallized Si formed in the annealed film could be ascribed to the excessive Mo atoms in the Mo/Si bilayer. It suggested that the thickness of Mo layer should be reduced, and the Si crystallization could appear after annealing. Interestingly, we found that the large grains with Mo_3Si phase had radial distribution in the film as the TEM magnification was decreased, as shown in Figure 4(c). As mentioned above, the Mo silicide consisting of $MoSi_2$, Mo_3Si, and Mo_3Si_2 could appear in this study. However, there was no formation of Mo_3Si_2 phase in the annealed sample. In previous researches [20, 21], the activation energies of $MoSi_2$ and Mo_3Si were estimated to be 204 and 223 kJ/mol, respectively, which were close to each other. Thus, in this study, $MoSi_2$ and Mo_3Si phases were formed sequentially.

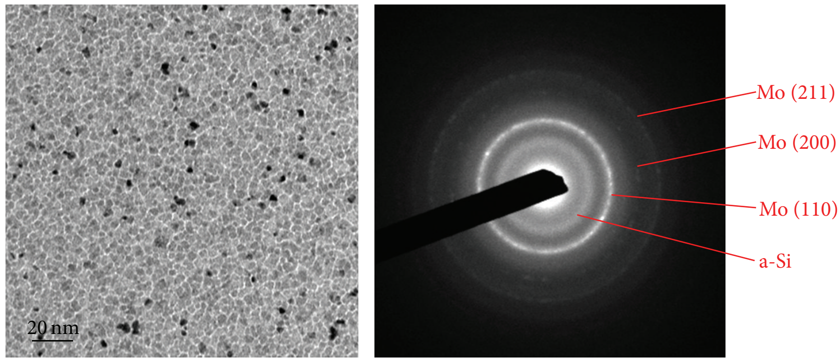

Figure 2: TEM bright field image and electron diffraction pattern of the as-deposited Mo/Si bilayer.

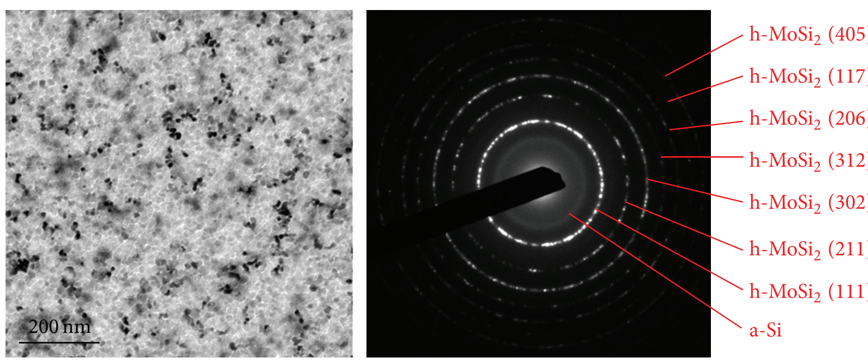

Figure 3: TEM bright field image and electron diffraction pattern of the 300°C-annealed Mo/Si bilayer.

Besides, the melting temperatures of $MoSi_2$ and Mo_3Si_2 were 1870 and 2190°C, respectively [22]. Commonly, the higher melting temperature of material would lead to a slower rate of formation. It can be speculated that the formation of Mo_3Si_2 is more difficult than $MoSi_2$. This could be the reason why Mo_3Si_2 phase did not appear in this study. Based on previous research [16], the difference in reflectivity resulted from the materials with different complex dielectric functions. In other words, the reflectivity of material can be changed via the phase transition process. Consequently, the decreased reflectivity of our sample (shown in Figure 1) with increasing the temperature from 255 to 425°C can be ascribed to the transition from Mo phase to h-$MoSi_2$ and Mo_3Si phases. Moreover, in this study, there is another factor to affect the sample reflectivity, that is, the grain feature of the sample. In Figure 2, the small and uniform grain size of as-deposited film can result in the reduction of optical anisotropy and lead to high reflectivity. However, as the Mo/Si bilayer was annealed at 450°C (Figure 4), the nonuniform grain size would induce optical anisotropy, which caused the lower reflectivity of the annealed films. Actually, the optical isotropy and anisotropy of materials are also related to the crystal structures. This implies that h-$MoSi_2$ and Mo_3Si structures could both possess optical anisotropy, leading to the decreased reflectivity.

The reflectivity spectra in the wavelength ranging from 350 to 1000 nm for as-deposited, 300°C-annealed and 450°C-annealed ZnS-SiO_2/Mo/Si/ZnS-SiO_2 samples are presented in Figure 5. For as-deposited sample, the reflectivity at a wavelength of 405 nm was measured to be 50.7%. After annealing at 300 and 450°C for 15 min, the reflectivities (at the wavelength of 405 nm) of these samples were decreased to 46.2% and 37.6%, respectively. The optical contrast is defined as $((R_1 - R_2)/R_1) \times 100$ %, where R_1 is the reflectivity of as-deposited state and R_2 is the reflectivity of annealed state. The optical contrast (at the wavelength of 405 nm) between as-deposited and 450°C-annealed Mo/Si films can be evaluated to 25.8%. It indicates that Mo/Si bilayer is suitable for BD-R application.

Figures 6(a) and 6(b) show the depth profiles measured by AES for as-deposited and 450°C-annealed Mo/Si films, respectively. Unlike the other annealing time of 15 min, the sample for AES measurement was only annealed for 3 min. In Figure 6(a), it was found that the film was composed by two layers, which were Mo layer and Si layer. After annealing at 450°C, the film was divided into three layers, that is, Mo layer, Mo-Si mixing layer, and Si layer. According to TEM observations, it can be confirmed that the Mo-Si mixing layer included the h-$MoSi_2$ and Mo_3Si phases. Additionally,

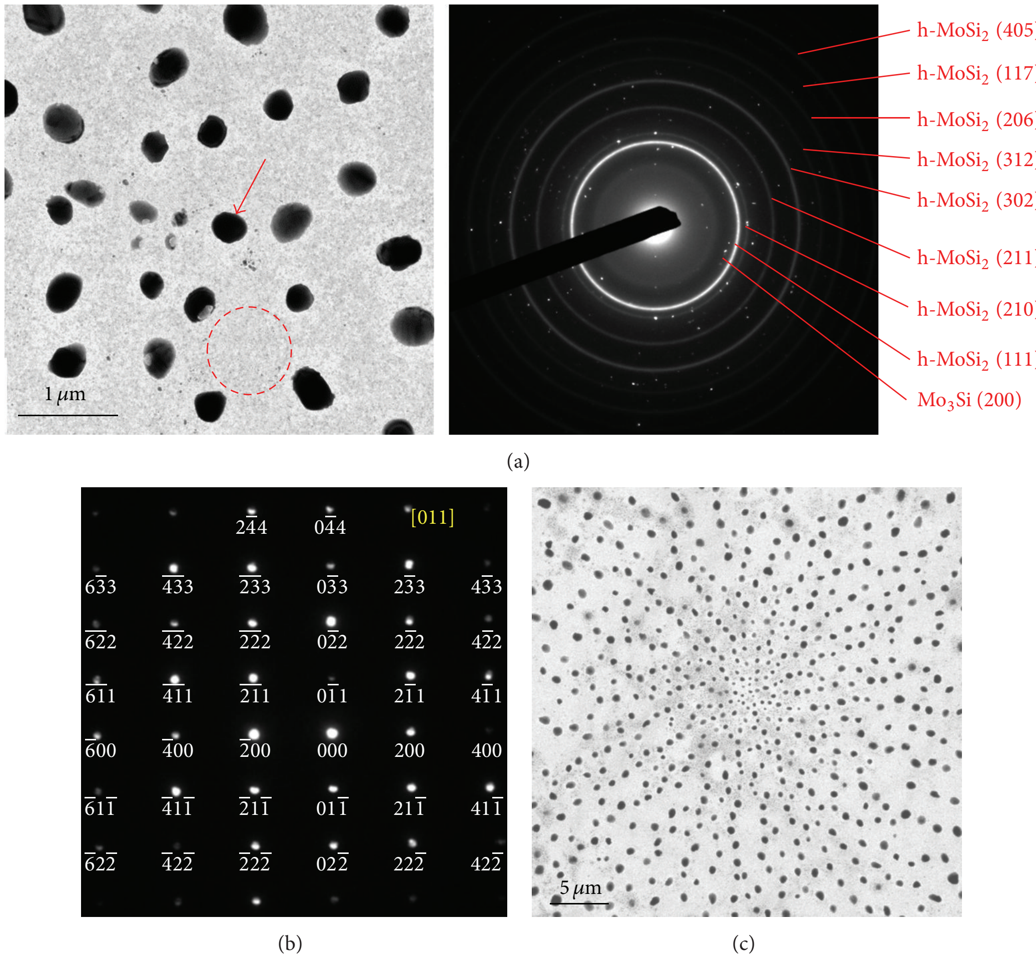

FIGURE 4: (a) TEM bright field image and electron diffraction pattern of the 450°C-annealed Mo/Si bilayer, (b) the SAED pattern of larger grain marked by an arrow in (a), and (c) TEM image with lower magnification.

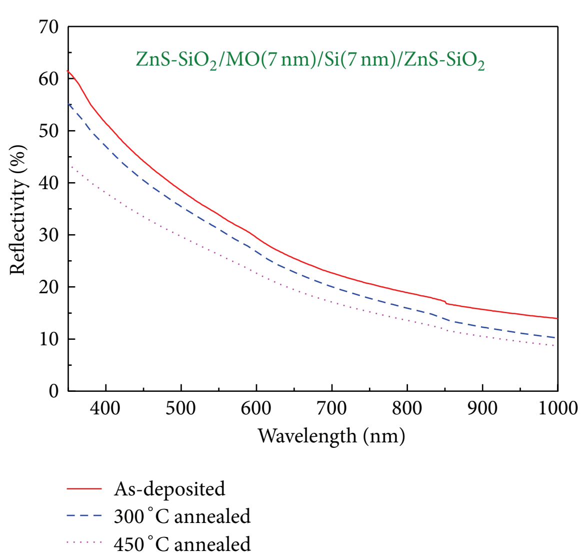

FIGURE 5: Variations of the reflectivity with wavelength for Mo/Si films at as-deposited, 300°C-annealed, and 450°C-annealed states.

the AES results revealed that the Mo silicide was formed by the interdiffusion of Mo and Si atoms, which was in good agreement with Holloway et al. research [17].

Figure 7 exhibits the dynamic test results that the jitter values and modulations vary with writing powers at 1× and 4× recording speeds. The suggested modulation and jitter value for BD-R should be larger than 0.4 and lower than 7%, respectively. As we can see, all measured modulations are larger than 0.4. From TEM results, the changes of structural phase and grain size uniformity in the as-deposited and annealed states would lead to high optical contrast. It probably results in enough modulation of the disc sample before and after laser writing. Experimental results show that the minimum jitter values are obtained to be 6.5% at 7.4 mW and 6.8% at 10.65 mW, respectively, for 1× and 4× recording speeds. It indicates that the Mo/Si bilayer has great potential in BD-R.

4. Conclusion

In summary, we have proposed a new BD-R containing Mo/Si recording layer. Thermal analysis shows that the Mo/Si bilayer

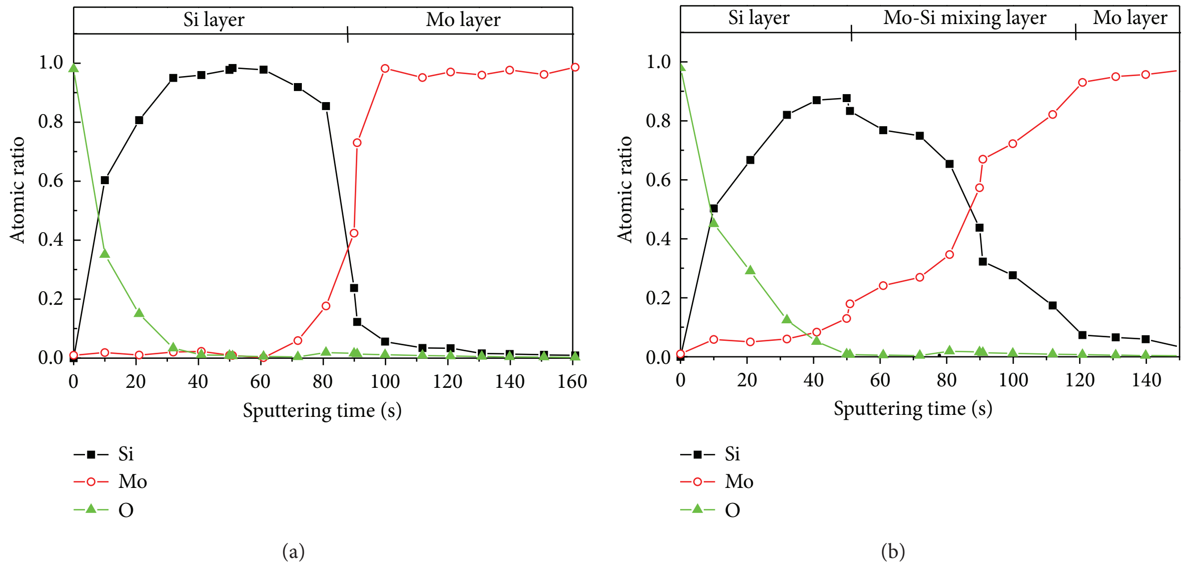

Figure 6: Element concentration depth profiles of (a) as-deposited and (b) 450°C-annealed Mo/Si bilayer samples.

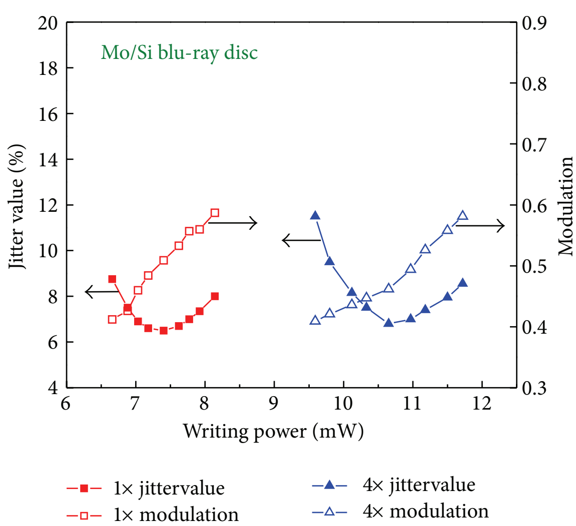

Figure 7: Jitter values and modulations as a function of writing power at the 1× and 4× recording speeds.

has a reflectivity change with the temperature ranging from 255 to 425°C. The Mo phase with grain size of 5 nm was found in the as-deposited film. After annealing at 300 and 450°C, the h-$MoSi_2$ and Mo_3Si were sequentially appeared. Due to the thicker Mo layer, there was no Si crystallization forming in the annealed film. The AES result confirmed that the formation of Mo silicide after annealing resulted from the interdiffusion of Mo and Si atoms. For 1× and 4× recording speeds, the optimum jitter values of 6.5% and 6.8% can be achieved at the recording powers of 7.4 and 10.65 mW, respectively. Obviously, the Mo/Si bilayer has great feasibility for write-once blue laser optical recording.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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