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Characterization and crystallization kinetics of sputtered NiSi thin films for blue laser optical recording application

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ABSTRACT

In this study, $Ni_{31}Si_{69}$, $Ni_{43}Si_{57}$ and $Ni_{63}Si_{37}$ thin films with the thickness of 16 nm were deposited at room temperature by co-sputtering using Ni and Si targets. From the result of reflectivity-temperature measurement, it was found the NiSi layers possessed two temperature ranges of reflectivity change, i.e. 150–270 °C and 320–370 °C. Microstructural analysis indicated that the $NiSi_2$ nano-crystalline phase was formed in the as-deposited state. After annealing at 270 and 500 °C, the crystallinity of $NiSi_2$ phase was improved and the Ni_2Si phase appeared, respectively. By measuring the optical reflectivity at a wavelength of 405 nm, the optical contrasts of these films before and after annealing at 270 °C were determined to be 24%, 16% and 26% with the Ni contents of 31, 43 and 63 at.%, respectively. The optimum jitter values of $Ni_{31}Si_{69}$ blu-ray disc were 7.7% at 5.7 mW and 8.2% at 7 mW, respectively, for 1× and 2× recording speeds. It reveals that the NiSi films have high potential in the application of blue laser recording media.

1. Introduction

In recent years, amorphous silicon (a-Si) has been widely adopted as the recording film of write-once optical disc because of its low cost and simple fabrication process. Nevertheless, its high crystallization temperature (700 °C) is a severe disadvantage for optical data storage. After that, the metal induced crystallization (MIC) technique was employed to decrease the crystallization temperature of a-Si [1–5]. In 2003, the Cu/a-Si bilayer was proposed to apply for the recording layer of write-once blu-ray disc [6]. Then various metal elements including Ni, Al, and Cu-Al alloy were presented as the metal layer in metal/Si bilayer system for the recording layer of blu-ray disc [7–9]. For the a-Si/Ni bilayer, the crystallization temperature of a-Si can be reduced to 350 °C. This is attributed to the formation of $NiSi_2$ phase with increasing the temperature to 150–250 °C, which can provide the nucleation sites for the crystallization of a-Si [7].

In our work, we have proposed the NiSi alloy thin film as a recording layer of write-once blu-ray disc. Moreover, the thermal property, optical characterization, crystallization mechanism and recording characteristic of NiSi film were investigated in detail. The composition of NiSi layer was modified by increasing the Ni element from 31 at.% to 63 at.%. The microstructures of NiSi films before and after annealing were identified by transmission electron microscopy (TEM).

2. Experimental

The 16-nm-thick NiSi thin films were grown on nature oxidized Si, glass and polycarbonate (PC) substrates at room temperature by co-sputtering using Ni and Si targets. The NiSi films were sandwiched with $ZnS\text{-}SiO_2$ protective layers. The sputtering power of Si target was fixed at 50 W; meanwhile the sputtering power of Ni target was varied from 40 to 70 W. As the sputtering powers of 40, 50 and 70 W for Ni target were selected, the corresponded compositions of NiSi layers were controlled to $Ni_{31}Si_{69}$, $Ni_{43}Si_{57}$ and $Ni_{63}Si_{37}$, respectively. A distance between the target and substrate

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was maintained at 10 cm. At a base pressure of 6.67×10^{-7} mbar, the Ar gas was introduced into the chamber, and the working pressure of film's growth was kept at 6.67×10^{-3} mbar.

For the dynamic tests, we adopted the on-groove recording method. The 1.1-mm-thick PC substrate with a 0.32-μm track pitch was employed to fabricate the blu-ray disc. Then the Ag reflective layer (90 nm), an upper dielectric layer of ZnS-SiO_2 (35 nm), the NiSi recording layer (16 nm) and a lower dielectric layer of ZnS-SiO_2 (24 nm) were deposited on the substrate in sequence. Finally, a 0.1-mm-thick PC transparent cover layer was covered on the top of these layers mentioned above by spin-coating. The layer structure of NiSi blu-ray disc is depicted in Fig. 1.

Thermal properties of the NiSi layers were analyzed by a home-made reflectivity-temperature analysis system from room temperature to 500 °C. The blue laser with a wavelength of 405 nm was used in the home-made instrument. Relationship between reflectivity and wavelength was measured using a UV–VIS–NIR spectrophotometer (Perkin-Elmer Lambda 900). The microstructures and crystallization mechanisms of these NiSi films were characterized by TEM. All samples for TEM measurements were prepared on the 3-mm-diameter copper meshes which fitted the TEM holder. Moreover, the crystal structure of the NiSi film was also determined by grazing incidence x-ray diffraction (XRD). In the XRD equipment, Cu K_α radiation ($\lambda = 1.5406$ Å) was employed as the source and Ge(220) was used as the monochromator. The compositions of NiSi films were confirmed by the electron probe micro-analyzer (EPMA). The jitter value and modulation of blu-ray disc were evaluated via a dynamic tester (ODU-1000, PULSTEC) and the testing conditions were shown in Table 1. A wavelength of 405 nm and the objective lens with a numerical aperture (NA) of 0.85 were applied for the measurements. The modulation code is (1, 7) RLL. The linear velocities of 1× and 2× recording speeds are 4.92 and 9.84 m/s, respectively.

3. Results and discussion

Fig. 2(a), (b) and (c) show the relationships between reflectivity and temperature of as-deposited $Ni_{31}Si_{69}$, $Ni_{43}Si_{57}$ and $Ni_{63}Si_{37}$ films, respectively. Various heating rates including 10, 20, 50 and 100 °C/min were chosen to perform the reflectivity-temperature measurements for the sake of estimation in activation energy, as discussed later. It can be observed that the NiSi layers have two temperature ranges of reflectivity change, i.e. 150–270 °C and 320–370 °C, and become almost constant until 500 °C. The reflectivity change with an increment of temperature reveals that the film possesses a structural change, resulting in the modification of its optical properties including reflectivity and transmittance [10]. The phase transition temperature of NiSi film can be defined as the temperature at a midpoint of reflectivity change. At the heating rates of 10, 20, 50 and 100 °C/min, the first and second phase transition temperatures of the $Ni_{31}Si_{69}$ film are 191 and 325 °C, 196 and 336 °C, 203 and 351 °C, and 211 and 362 °C, respectively. Meanwhile, the first and second phase transition temperatures of the $Ni_{43}Si_{57}$ film measured at these four heating rates are 203 and 333 °C, 209 and 342 °C, 218 and 356 °C, and 222 and 366 °C, respectively. Additionally, the first and second phase transition temperatures of the $Ni_{63}Si_{37}$ film (at these four heating rates) are also determined to be 218 and 341 °C, 223 and 350 °C, 230 and 362 °C, and 236 and 372 °C, respectively. In general, the phase transition temperature (or crystallization temperature) of 150–400 °C for the material is very suitable to optical recording. It indicates that the material owns both enough thermal stability and relatively low writing power as the optical disc is recorded. We can also find that the phase transition temperatures of these three NiSi films increased as the amount of Ni element was increased, which implied the thermal stability was improved with increasing the Ni amount. According to the result, we chose the annealing temperatures of 270 and 500 °C to examine the microstructures of NiSi films.

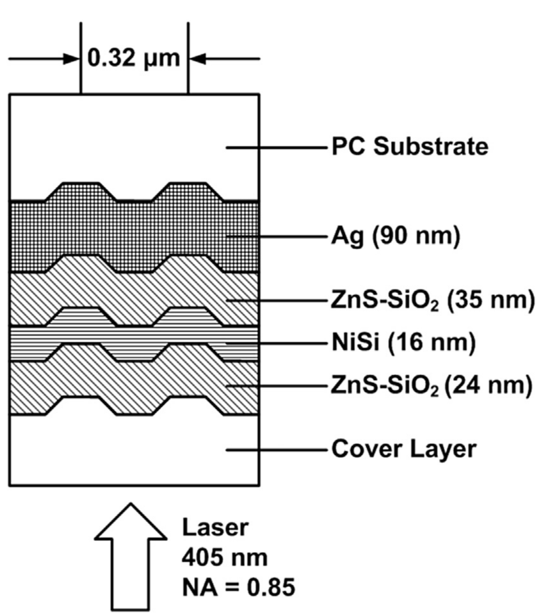

Figure 1. Layer structure of the NiSi write-once blu-ray disc.

Table 1
Dynamic test conditions.

User capacity	25 GB
Substrate thickness	1.1 mm
Wavelength	405 nm
Numerical aperture	0.85
Modulation code	(1,7) RLL
Track pitch	0.32 μm
Linear velocity	4.92 m/s (1 ×), 9.84 m/s (2 ×)
Recording format	On-groove

Fig. 3(a) exhibits the TEM image and selected area electron diffraction (SAED) pattern of as-deposited $Ni_{31}Si_{69}$ film. It can be seen that the uniform and small grains with the size about 3–5 nm appeared in the as-deposited NiSi film. From the diffraction pattern, the un-obvious rings indexed to (111) and (220) planes of $NiSi_2$ phase were observed. It is speculated that the $NiSi_2$ phase could appear in the as-deposited NiSi film after depositing at specific conditions (sputtering power, growth pressure, and so on). However, it should be mentioned that although the $NiSi_2$ phase can appear in the as-deposited film, this phase was actually formed with many small grains and possessed a very weak crystal quality. In other words, the $NiSi_2$ formation in the as-deposited film is the nano-crystalline phase. Fig. 3(b) displays the TEM image and SAED pattern of 270 °C-annealed (15 min) $Ni_{31}Si_{69}$ film. For the observation of TEM plane-view, the grain size was increased to 5–10 nm. With regard to the $NiSi_2$ phase, the new ring pattern of (200) plane appeared. Moreover, we found the other diffraction rings of $NiSi_2$ phase ((111) and (220) planes) became more obvious, indicating that the crystallinity of $NiSi_2$ phase was enhanced after annealing at 270 °C. In addition, the other phase of nano-crystalline NiSi with weak diffraction ring was also observed in the 270 °C-annealed film. Apparently, the reflectivity reduction in 150–270 °C was mainly attributed to the improvement in $NiSi_2$ crystallinity, as shown in Fig. 2. On the other hand, the $NiSi_2$ nano-crystalline phase with a very weak crystal quality appeared in the as-deposited film,