Effects of Sputter Order and Oxide Layer on Amorphous Formation of Zr-Ni Thin Film System

Masahiro Kitada and Fumiyoshi Kirino

Graduate School of Fine Arts, Tokyo National University of Fine Arts and Music, Tokyo 110-8714, Japan

Effects of the sputtering order and the presence of an oxide layer on an amorphous metal layer formation of zirconium-nickel bilayer thin films annealed at 623 K (350°C) have been investigated. Nickel species are found to diffuse preferentially from the nickel layer into the zirconium layer in Zr/Ni bilayer thin film. From this diffusion, the amorphous phase and voids are formed. However, by the change of the sputtering order and with the formation of a Zr oxide layer, the amorphous and voids are not formed. This indicates that nickel species migrate into the amorphous layer by means of vacancies. Vacancies are supplied from the zirconium-free surface.

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1. Introduction

Amorphous phases are formed by various means, for example, rapid quenching,¹⁾ irradiation,²⁾ co-sputtering,³⁾ interdiffusion⁴⁾ and others.^{5–7)} On the other hand, recently a bulk amorphous alloy has been extensively developed as a metallic glass.⁸⁾ Amorphous phase formation in multilayer thin films by solid-state diffusion is very important in thin film device application as it affects various characteristics of devices, for example, their reliability and the device yield.⁹⁾ The amorphous phase formation can be observed by a transmission electron microscope.¹⁰⁾

In the zirconium-permalloy bilayer thin film system, the amorphous phase is formed by interdiffusion between the films and Kirkendall voids are produced by preferential diffusion of Ni species.¹¹⁾ To produce the void, it is necessary that many vacancies migrate to the permalloy thin film side from the Zr thin film side. However, the supply source of vacancies has not been confirmed. Changing the position of the bilayer thin film, the diffusion path, the formation of diffusion barrier, and other parameters of the diffusion system are effective strategies that can be employed to clarify the vacancy source or diffusion mechanism. Since the diffusion behavior of Zr-permalloy system is very complex, a Zr-Ni system was chosen as a simpler case.^{12–14)}

In this paper the effects of the sputtering order and of the presence of an oxide layer on the Zr-Ni thin film system are described.

2. Experimental Details

Zr-Ni thin films were prepared using a conventional rf-sputtering system. The ultimate vacuum before sputtering was 10^{-5} Pa. The target material purities were 99.99 mass%. The substrate was Corning No. 7059 glass. The substrate was heated to 473 K (200°C) to sputter the underlayer and maintained under 323 K (50°C) during the upper layer sputtering to avoid a reaction between the films. The film thicknesses were approximately 50 nm for Zr and 25 nm for Ni. If necessary, oxide layers were formed on Ni and Zr by introducing six-nine purity gas into the vacuum chamber. Ni and Zr oxide layers were naturally grown as six-nine purity

oxygen gas was introduced into a vacuum chamber. The oxidation time was 3600 s (1 h). After sputtering, the films were annealed at 623 K (350°C) for 3600 to 7200 s (1 to 2 h) in the sputtering chamber in a vacuum of 10^{-5} Pa.

The cross sectional microstructure of the specimens was observed by means of transmission electron microscopy. The specimens were finally thinned by ion etching.

Depth-composition profiles were obtained by AES. The depth for AES measurement was obtained from the sputtering rate. The composition of the mixed layer was determined by EDX attached to the transmission electron microscope.

3. Results and Discussion

3.1 Zr/Ni thin film

Cross-sectional transmission electron micrograph of Zr/Ni(glass substrate) system after annealing at 623 K (350°C) for 3600 s (1 h) is shown in Fig. 1. By the reaction between the films, four regions were observed in the cross-section. The top region is approximately 18 nm in thickness and is unreacted Zr and shows crystallographic contrast. No Ni

Fig. 1 Cross sectional transmission electron micrograph of Zr/Ni bilayer thin film annealed at 623 K (350°C) for 3600 s (1 h). A, C, V and G indicate amorphous, crystal, void and glass substrate, respectively.

Fig. 2 Electron diffraction pattern of the amorphous region shown in Fig. 1.

Fig. 3 Typical EDX spectrum of the mixing layer shown in Fig. 1.

species were detected in this layer by EDX. Since the electron diffraction pattern obtained from the second region is a halo, as shown in Fig. 2, the region is amorphous. Its thickness was approximately twice that of the unreacted Zr layer. The third region between the amorphous region and the Ni layer was Ni rich phase (about Ni-10 mol% Zr, as obtained by EDX) and shows very small crystal size of 5 to 6 nm in diameter. The fourth 15 nm thick region is what remains from the 25 nm that was deposited. This region contains several voids. The typical EDX spectrum of the second amorphous region is shown in Fig. 3. From the spectrum it is clear that the amorphous region is a mixture of Ni and Zr. It is thought that the voids were due to a preferential diffusion of Ni species towards the mixing layer by a vacancy-like mechanism. Inversely, vacancies migrated to the Ni layer from the Zr layer. In all respects, the Kirkendall diffusion occurred in the thin film system.

Depth-composition profiles for Zr/Ni film annealed at 623 K (350°C) for 3600 s (1 h) are shown in Fig. 4. The relative concentration of Zr decreases monotonically with increasing depth. However, the curve for Ni was not monotone and shows a peak near the third region as mentioned above. Then the concentration rapidly decreased in the Ni layer. A possible cause of the Ni decrease is due to void formation. The average concentration of Zr at the middle point in the amorphous region was 73 mol%, as determined by EDX. Since the Ni concentration in the thin third region corresponding to the peak position of Ni is sufficiently high (approximately Zr-85 mol% Ni), the amor-

Fig. 4 Depth-composition profiles for Zr/Ni bilayer thin film annealed at 623 K (350°C) for 3600 s (1 h).

Fig. 5 Cross sectional transmission electron micrograph of Zr/Ni bilayer thin film annealed at 623 K (350°C) for 7200 s (2 h). A, V and G indicate amorphous, void and glass substrate, respectively.

phous phase was not formed.

The cross-sectional transmission electron micrograph of Zr/Ni thin film after annealing at 623 K (350°C) for 7200 s (2 h) is shown in Fig. 5. The most of the Ni layer contains large voids as a result of vacancy flow and only narrow nickel bridges between the substrate and the amorphous layer were observed.

3.2 Ni/Zr thin film

The Ni/Zr/(glass-substrate) system was examined to clarify the role of vacancies supplied from the Zr surface. The cross sectional transmission electron micrograph of the specimen annealed at 623 K (350°C) for 3600 s (1 h) is shown in Fig. 6. Although a large quantity of the amorphous phase observed in the Zr/Ni system as shown in Fig. 1, the Ni/Zr bilayer film did not show the amorphous phase. In this system, the vacancy is not supplied from the Zr film side because the film is in contact with the glass substrate. That is, it is necessary that the vacancy is supplied from the free surface of the Zr layer to form the amorphous phase. The vacancy supplied from the Zr surface assists the Ni preferential diffusion towards the Zr.

Fig. 6 Cross sectional transmission electron micrograph of Ni/Zr bilayer thin film annealed at 623 K (350°C) for 3600 s (1 h). G indicates glass substrate.

Fig. 7 Lattice image near boundary between the Ni and the Zr for Ni/Zr bilayer thin film annealed at 623 K (350°C) for 3600 s (1 h).

However, a small amount of amorphous phase was confirmed near the boundary between Ni and Zr layers in a high-resolution transmission electron micrograph. The lattice image near the boundary is shown in Fig. 7. The amorphous phase is observed here and there near the boundary. It is thought that the amorphous formation is due to vacancies and vacancy sources like dislocations contained in the Zr thin film.

3.3 Zr/(Ni-oxide)/Ni film

Zr/(Ni-oxide)/Ni/(glass-substrate) film was obtained by surface oxidation of Ni at room temperature for 3600 s (1 h) before sputtering Zr. A cross-sectional transmission electron micrograph of Zr/(Ni-oxide)/Ni annealed at 623 K (350°C) for 3600 s (1 h) is shown in Fig. 8. The amorphous layer grew and the Ni-oxide layer did not interrupt the diffusion of Ni species into the Zr layer. However, no voids were observed in the Ni layer.

Depth composition profiles of Zr/(Ni-oxide)/Ni film after annealing are shown in Fig. 9. The relative concentration of

Fig. 8 Cross sectional transmission electron micrograph and electron diffraction pattern of Zr/(Ni-oxide)/Ni thin film annealed at 623 K (350°C) for 3600 s (1 h). A and G indicate amorphous and glass substrate, respectively.

Fig. 9 Depth-composition profiles for Zr/Ni-oxide/Ni thin film annealed at 623 K (350°C) for 3600 s (1 h).

Ni in the amorphous layer was low in comparison with that of Zr/Ni system shown in Fig. 4. Although the oxygen peak was observed in the as-sputtered specimen, the peak was annihilated after annealing. That is, the Ni oxide decomposed and the oxygen species diffused preferentially into the Zr layers.

The typical composition of the amorphous layer obtained by EDX was approximately Zr-23 mol%Ni. This is lower than that of the amorphous phase for annealed Zr/Ni thin film. It is therefore thought that the vacancy flow into the Ni layer is small in comparison with the case of Zr/Ni thin film.

3.4 Effect of Zr-oxide layer

(Zr-oxide)/Zr/Ni/(glass-substrate) film was obtained by oxidation of the surface of Zr film at room temperature for 3600 s (1 h) before annealing. A cross-sectional transmission electron micrograph of the (Zr-oxide)/Zr/Ni film annealed at 623 K (350°C) for 3600 s (1 h) is shown in Fig. 10. Although Zr and Ni crystal grains were observed, the amorphous phase was not observed. The supply of vacancy from the Zr surface was suppressed by the Zr-oxide layer, and the preferential Ni diffusion into the Zr layer did not occur. Therefore, the amorphous phase and voids did not grow.

Fig. 10 Cross sectional transmission electron micrograph of (Zr-oxide)/Zr/Ni thin film annealed at 623 K (350°C) for 3600 s (1 h).

Fig. 11 Depth-composition profiles for Zr/(Zr-oxide)/Ni thin film annealed at 623 K (350°C) for 3600 s (1 h).

The Zr/(Zr-oxide)/Ni film also did not form the amorphous phase or voids. Migrations of Ni species and vacancies were interrupted by the Zr oxide layer because the oxide did not decompose. In the depth composition profile, the oxygen peak was detected after annealing, shown in Fig. 11.

No amorphous phase was observed in Ni/(Zr-oxide)/Zr thin film in the high-resolution electron micrograph. This is due to the lack of vacancy supply and barrier effect of the oxide.

The sputtering order and the oxide layer had a strong influence on the amorphous and void formations, as mentioned above. To form voids, a large number of vacancies must migrate towards the Ni underlayer side from the upper Zr thin film side. Although the sputter films contain

many vacancies, this is not sufficient for the formation of large voids as shown in the present results. Lattice defects, such as dislocations and grain boundaries in the Zr thin films, also contribute as the supply source of vacancies to form the voids. However, these defects also can not make such large voids as shown in the present results. It is therefore thought that the vacancies are supplied from the free surface. When the free surface is clean, the vacancy is able to be supplied from the surface. However, the supply is prevented by the surface oxide layer of the Zr thin film.

On the other hand, many vacancies migrate towards the Ni underlayer and form voids. This phenomenon shows that vacancies aid the migration of Ni species in the amorphous phase. That is, the preferential diffusion of Ni species into the Zr layer is promoted by vacancy-like defects in the amorphous layer.

4. Conclusion

The effects of oxide layer and sputtering order of Zr-Ni thin films on the amorphous phase and void formations were studied. Although the amorphous and voids are observed in Zr/Ni thin films, these were not observed in (Zr-oxide)/Zr/Ni and Ni/Zr thin films. This indicates that the nickel species migrate preferentially with the assistance of vacancy into the amorphous layer and vacancies are supplied from the zirconium free-surface.

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