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Reactions between zirconium/permalloy bilayer thin films

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The interdiffusion and reactions of zirconium/permalloy bilayer thin films annealed at 150 to 350 °C were investigated. Nickel atoms preferentially diffuse from the permalloy layer into the zirconium layer. This preferential diffusion results in the growth of an amorphous phase between the zirconium and permalloy thin films. Consequently, the magnetic properties of the permalloy thin layer in the bilayer thin films change. The starting temperature of interdiffusion between zirconium and permalloy films is higher than that of a titanium/permalloy system reported previously.

1. Introduction

Zirconium/permalloy bilayer thin films have been investigated as a current shunt to the permalloy layer to generate a biasing magnetic field. A conventional magnetoresistive element uses titanium/permalloy bilayer thin films [1, 2]. However, the magnetic properties change due to the reaction between permalloy and titanium thin films [3–5]. For example, the coercivity and electrical resistivity of the permalloy layer in the bilayer films begin to increase when the annealing temperature is over 225 to 250 °C [6]. In specimens annealed at 400 to 500 °C, the intermetallic compounds $TiFe_2$, Ti_2Ni, and $TiNi_3$ are formed [4]. This compound formation and interdiffusion give the bilayer thin films a very high coercivity. To use a higher temperature fabrication process and obtain a more reliable bilayer thin film, the starting temperature of the interdiffusion must be increased. This paper describes interdiffusion and reaction between zirconium and permalloy thin films.

2. Experimental procedure

Zirconium/permalloy bilayer thin films were prepared by conventional electron-beam deposition in a magnetic field. The permalloy source composition was Ni–19 wt % Fe. The source material purities were 99.95 wt % for iron, 99.9 wt % for nickel, and 99.9 wt % for zirconium. The substrate, Corning no. 7059 glass, was heated to 230 °C for permalloy evaporation and to 50 to 100 °C for zirconium evaporation. The zirconium deposition temperature was selected to prevent the films reacting together and to avoid the bilayer film separating from the substrate. The films were approximately 40 nm thick for the permalloy, and 100 nm thick for zirconium, as determined with a talystep. The bilayer thin films were deposited continuously in a vacuum of 10^{-4} Pa, and annealed in a vacuum of 10^{-4} Pa for 1 to 3 h at 150 to 350 °C.

The evaporated permalloy film composition was between Ni–19 wt % Fe and Ni–20 wt % Fe, which was confirmed by inductively coupled plasma-emission spectroscopy (ICPS).

The magnetic properties were measured with a vibrating sample magnetometer and a *B–H* looper. Depth–composition profiles were obtained by secondary ion mass spectrometry (SIMS). The concentration was calibrated using values measured by ICPS for specimens of known composition prepared by co-sputtering. The depth was obtained from sputtering rate measurements.

The cross-sectional microstructure was observed using transmission electron microscopy. The specimens were deposited on to the Corning no. 7059 glass substrate and finally thinned by ion etching.

3. Results and discussion

3.1. Coercivity change of permalloy thin films

The easy-magnetization-direction coercivities of the permalloy layers in the bilayer thin films are shown in Fig. 1. Values are for both as-deposited specimens and for specimens annealed at 175 to 310 °C for 1 h in a vacuum. The coercivities of the permalloy layer did not change with annealing at 175 to 290 °C, but after annealing at 300 °C, a slight increase in coercivity was detected. The coercivities of the permalloy thin films annealed above 300 °C increased rapidly, and the bilayer thin films became magnetically semi-hard or

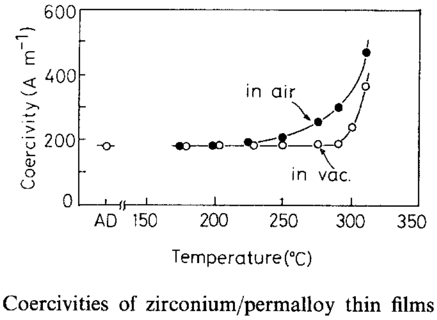

Figure 1 Coercivities of zirconium/permalloy thin films annealed for 1 h. AD, as-deposited specimen.

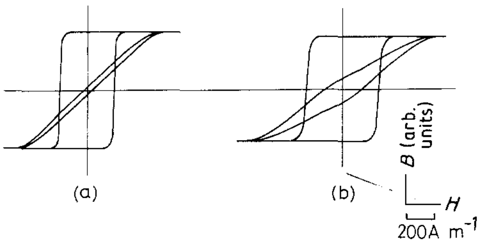

Figure 2 Magnetic hysteresis loops of zirconium/permalloy thin films, (a) as-deposited, (b) annealed at 300 °C.

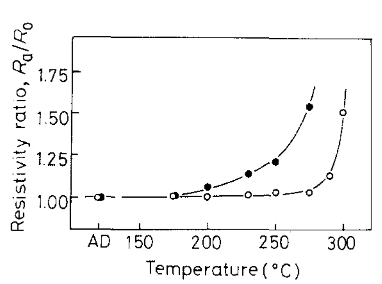

Figure 4 Change in electrical resistance ratio, R_a/R_0, for annealed zirconium/permalloy bilayer thin films.

hard. These results clearly show that the permalloy layer in the bilayer thin films lost its soft magnetic properties as a result of the interdiffusion.

Magnetic hysteresis loops of the as-deposited and annealed specimens are shown in Fig. 2. In the loop of the bilayer thin film annealed at 300 °C for 1 h, the saturation magnetization decreased slightly and the coercivity increased, probably as a result of the interdiffusion and/or reaction. Although the apparent shape of the magnetic hysteresis loop for the easy-magnetization-direction was unchanged, the shape for the hard magnetization direction did change. The hard-magnetization-direction coercivity also increased. The specimen annealed above 350 °C for 1 h had a step-like hysteresis loop. This is probably due to interdiffusion forming a magnetically hard layer. In this specimen, the hard-magnetization-direction coercivity much increased.

3.2. Electrical resistivity

The dependence of electrical resistivity of the zirconium thin films on the film thickness is shown in Fig. 3. The electrical resistivity increased as the film thickness decreased to below 140 nm. The resistivities of 140 to 300 nm thick films were approximately $85 \times 10^{-8}\,\Omega$m. The film thickness dependence of the resistivity under 140 nm thick was approximately given by the Fuchs law. The value probably depends on source purity, vacuum during deposition, and other factors.

The changes in the electrical resistance ratio, R_a/R_0, for annealed zirconium/permalloy bilayer thin films are shown in Fig. 4. Here, R_0 represents as-deposited resistivity and R_a represents annealed resistivity. The resistance change is first observed at 290 °C, and the value increases rapidly with increasing annealing temperature. The electrical resistances of both the permalloy and zirconium single layer films barley increase under these annealing conditions. Although grain growth was observed on annealing over 275 °C annealing, the growth does not contribute to the increase in electrical resistivity. Therefore, the increase in resistivity in bilayer thin films is obviously due to the interdiffusion between zirconium and permalloy layers. The starting temperature of the resistivity increase agreed well with that of the coercivity increase. The starting temperature of the zirconium/permalloy bilayer thin film is higher than that of the titanium/permalloy system [6].

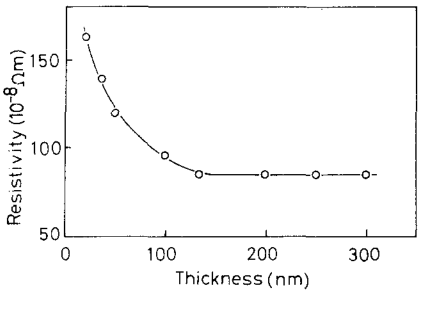

Figure 3 Dependence of electrical resistivity of zirconium thin films on film thickness.

3.3. Microstructural change

A cross-sectional transmission electron micrograph of the as-deposited zirconium/permalloy bilayer thin film is shown in Fig. 5a. Permalloy grains with an average diameter of approximately 10 nm were observed and no texture was evident. Columnar zirconium grains grew and the average grain diameter measured parallel to the substrate plane was approximately 20 nm. Randomly oriented very fine zirconium grains were noted near the permalloy layer. Therefore, no reaction occurred between the zirconium and permalloy layers in the as-deposited condition.

Clear microstructural change, namely amorphous-like layer growth, was observed in the specimen after annealing above 325 °C. A cross-sectional transmission electron micrograph of the specimen annealed at 350 °C is shown in Fig. 5b. The image contrast of the growth layer did not change when the thin film specimens were tilted. Microbeam diffraction of the amorphous-like layer did not give a clear electron diffraction pattern. Therefore, it is thought that the layer is an amorphous phase formed by interdiffusion. The permalloy and zirconium grains also grew during annealing, as shown in Fig. 5b.

Growth of an amorphous phase by interdiffusion in a Ni–Zr system has been previously reported [7, 8]. In that system, the amorphous phase grows by preferential diffusion of the nickel atoms and by bulk diffusion through the amorphous layer. In the titanium–permalloy [6] and Ti–Ni systems [9], similar preferential diffusion of nickel species and amorphous phase formation were observed by SIMS and cross-sectional electron microscopy, respectively. Preferential nickel diffusion produces many micro-voids in the permalloy layer near the substrate, as shown in Fig. 5b. This agreed well with the previous result [10].

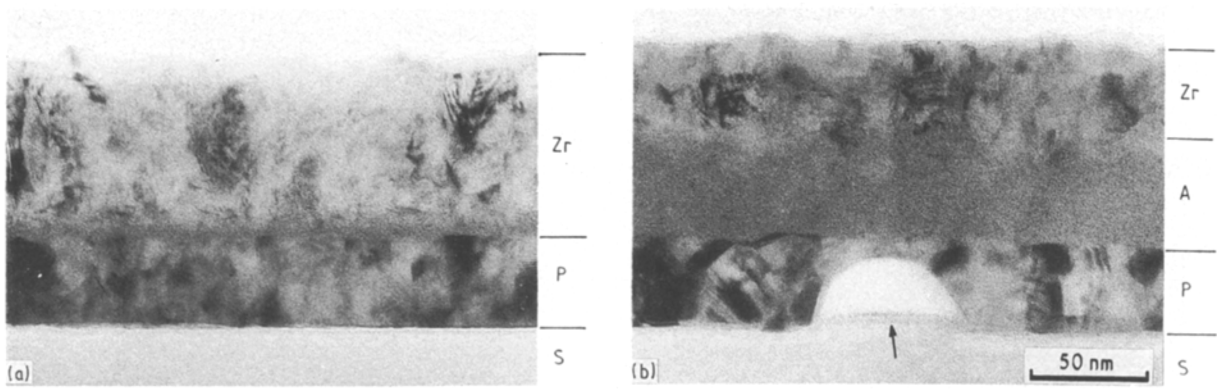

Figure 5 Cross-sectional transmission electron micrographs of zirconium/permalloy bilayer thin films, (a) as-deposited and (b) annealed at 350 °C. P, A, S, and arrow indicate permalloy, amorphous, substrate, and void, respectively.

A cross-sectional transmission electron micrograph of the zirconium/permalloy bilayer thin film after annealing at 400 °C shows crystalline layers between the zirconium and the permalloy thin films. The detailed structure of the reacted layer will be shown elsewhere.

3.4. Depth–composition profile

Depth–composition profiles for zirconium/permalloy bilayer thin films are shown in Fig. 6. The profiles for as-deposited bilayer thin film, in Fig. 6a, show separated composition profiles for zirconium and nickel (or iron). It is, therefore, thought that no interdiffusion occurred in the as-deposited specimen. In fact, the magnetic and electric properties of the permalloy layer did not change either before or after zirconium deposition.

After annealing at 300 °C for 1 h, interdiffusion was observed in the profiles. In particular, nickel species diffused preferentially into the zirconium layer. This preferential diffusion has previously been observed in a Zr–Ni system [7, 8], and also in a titanium–permalloy system [4, 6]. Because no grain-boundary diffusion was observed in the electron micrographs, the preferential diffusion may be a bulk phenomenon.

The preferential diffusion into the zirconium layer was enhanced for the specimen annealed at 350 °C. The iron species did not diffuse into the titanium layer. Therefore, the bulk-diffused nickel atoms formed amorphous phases. The calibrated composition of the amorphous layer obtained from the depth–composition profile, as shown by arrow A in Fig. 6, is approximately $Ni_{0.27}Zr_{0.73}$. This composition is in the amorphous formation range estimated by free energy calculation and by mechanical alloying experiments [11].

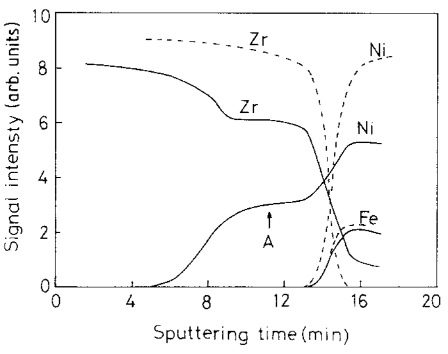

Figure 6 Depth–composition profiles for as (- - - -) as-deposited, and (——) annealed (at 350 °C for 1 h) Zr/Permalloy bilayer thin films. Arrow A indicates composition-estimation depth for amorphous layer.

3.5. Effect of annealing atmosphere

The influence of annealing atmosphere during interdiffusion and reaction for zirconium/permalloy bilayer thin films was studied. The electrical resistivity of zirconium/permalloy bilayer thin films annealed in air is shown in Fig. 4. The resistivity increase started at 225 °C, which is approximately 75 °C lower than that of the specimen annealed in vacuum. It is considered that diffused oxygen species in the zirconium layer increased the electrical resistivity. The coercivity of the films annealed in air also changed at a lower temperature than for the vacuum-annealed specimen, as shown in Fig. 1. Therefore, the oxygen promoted the interdiffusion and/or reaction.

In the depth–composition profile of the specimen annealed at 250 °C in air, the nickel diffusion distance of the air-annealed specimen was greater than that of the vacuum-annealed specimen. The oxygen species diffused to the permalloy layer. Therefore, the oxygen atoms assisted the mixing of nickel and zirconium atoms and perhaps also the amorphous phase formation. The detailed effect of oxygen on amorphous formation will be reported elsewhere.

4. Conclusions

In a zirconium–permalloy thin film system, nickel atoms preferentially diffuse from the permalloy into the zirconium layer. This interdiffusion leads to the formation of an amorphous-like phase. The magnetic properties of the permalloy layer in the zirconium/permalloy bilayer thin films are generated by the interdiffusion. The starting temperature of coercivity increase for zirconium/permalloy bilayer films is higher than that of titanium/permalloy system.

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