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Internal Stress in Ferrite Plated Thin Films

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Abstract: Internal stress in ferrite plated films of Fe_3O_4 and Ni-ferrite was evaluated, and its dependence on the plating conditions was investigated. The internal stress was estimated to be $0.5\sim 1.7\times 10^9$ dyn/cm² in tension. For Ni-ferrite films, the stress increased with increasing the atomic ratio of Ni/Fe in reaction solution. The plated films were composed of columnar-shaped grains of $0.2\sim 0.3\mu\text{m}$ in size near the top surface as observed by SEM. Crystallinity of the films degraded with increasing Ni/Fe, and peaks of spinel structure were not observed by X-ray diffraction diagram for Ni/Fe=0.83. These results suggest that excess Ni ions in the reaction solution increase impurities in the films, which may increase the tensile internal stress. We found that the internal stress can be reduced by adjusting layout of sprays (i.e. changing the height of the nozzles from the table) in the spin-spray ferrite plating.

1. INTRODUCTION

Ferrite plating is an excellent method for preparing magnetic thin films of spinel oxides from an aqueous solution at low temperature below 100°C[1]. However, adhesion of the films to the substrates is generally weak. When their thickness exceeded several microns, the films peeled off. The plated films are composed of large columnar-shaped grains, as observed by SEM. The structure is very similar to that of films sputter-deposited at high working gas pressure[2]. In general, the films composed of such separate columns have tensile internal stress which tend to cause delamination, resulting in the peeling off of the films when they become thick[3-4]. In this study, we evaluated the internal stress in Fe_3O_4 and Ni-ferrite films and investigated the dependence of the stress on the plating conditions.

2. EXPERIMENTAL

Films of Fe_3O_4 and Ni-ferrite films, $0.4\sim 0.6\mu\text{m}$ in thickness, were prepared on $25\mu\text{m}$ thick polyimide sheets by spin-spray ferrite plating method[5] at 85°C and pH of 6~7. The reaction solution of $\text{FeCl}_2+\text{NiCl}_2$ and the oxidizing solution of $\text{NaNO}_2+\text{CH}_3\text{COONH}_4$ were simultaneously sprayed onto the substrates on the spinning table from two nozzles. Both nozzles were set at the same height h from the rotating substrates. To change the spraying conditions, we chose two values $h=100$ and 130mm . Residual internal stress was estimated by measuring the warp of the sheets after the deposition. Crystallographic properties of the films were evaluated by X-ray diffractometry (XRD) using $\text{CuK}\alpha$ radiation. Cross sections of the films were observed by SEM.

3. RESULTS AND DISCUSSION

Figure 1 shows the dependence of the internal stress on atomic ratio of Ni/Fe in the reaction solution for the two values of h . The stress in the films was estimated to be $5\sim 7\times 10^8$ dyn/cm² in tension for Ni/Fe=0~0.5, and it increased rapidly for Ni/Fe above 0.5. The value reached 1.7×10^9 dyn/cm² for Ni/Fe=0.70 and $h=130\text{mm}$. For Ni/Fe above 0.5, the internal stress for

$h=100\text{mm}$ was smaller than that for $h=130\text{mm}$. When $\text{Ni/Fe}>1$, cracks were caused in the films, which peeled off in part from the substrates. Because adhesion of these films to the substrates was weaker than the tensile internal stress which tends to remove the films from the substrates.

Crystallinity degraded with increasing Ni/Fe in the region above 0.5 as shown in X-ray diffraction diagram of Fig.2 for the Ni ferrite films prepared at $h=100\text{mm}$. The films prepared at $\text{Ni/Fe}=0.42$ have the (111) texture, while peaks of spinel structure were indiscernible for the films prepared at $\text{Ni/Fe}=0.83$. This indicates that crystallinity degraded and amorphous region in the films increased with increasing Ni/Fe . Excess Ni in the reaction solution may become nuclei of impurities in the films, which degrade the crystallinity.

The plated films were composed of columnar-shaped grains of $0.2\sim0.3\mu\text{m}$ in size near the top surface as observed by SEM. Topographical changes were not observed in the films prepared at $\text{Ni/Fe}>0.5$, but the crystallinity degraded and the internal stress increased with increasing Ni/Fe . This suggests that the internal stress in these films is influenced by crystallinity.

The internal stress increased with increasing the spray height h as already shown in Fig.1. In the case that the sprays are located far from the substrates, before the reaction solution reaches the substrates, mixture between the reaction solution and the oxidizing solution may make impurity particles. These impurities are contained in the plated films and degrade the crystallinity. Since the ferrite plated films with poor crystallinity have larger tensile internal stress as mentioned above, the films plated under the conditions that h is larger have larger internal stress.

4. CONCLUSION

Internal stress in ferrite plated films of Fe_3O_4 and Ni-ferrite prepared by spin-spray ferrite plating method was estimated to be $0.5\sim1.7\times10^9\text{ dyn/cm}^2$ in tension. The stress increased with increasing atomic ratio Ni/Fe in the reaction solution. The plated films were composed of columnar-shaped grains of $0.2\sim0.3\mu\text{m}$ in size near the top surface as observed by SEM, however, the grain size did not change with Ni/Fe . X-ray diffractometry showed that crystallinity of the films with large tensile stress was poor. These results indicate that one of the reasons of the tensile internal stress in the ferrite plated films is the existence of poor crystalline or amorphous region which excess Ni ions cause. The internal stress in the ferrite plated films may reflect the degree of the crystallinity more than the topographical properties. We found that the internal stress decreased by reducing the height of the spray nozzles. This suggests that optimizing the layout of the sprays in the spin-spray ferrite plating apparatus enables us to make ferrite films with smaller internal stress and better crystallinity.

References

- [1] M. Abe and Y. Tamaura, J. Appl. Phys., **55** (1984) 2614-2616.
- [2] J. A. Thornton, J. Vac. Sci. Technol., **11** (1974) 666-670.
- [3] D. W. Hoffman and J. A. Thornton, J. Vac. Sci. Technol., **20** (1982) 355-358.
- [4] J. A. Thornton, J. Vac. Sci. Technol., **A4** (1986) 3059-3065.
- [5] M. Abe, Y. Tamaura, M. Oishi, T. Saitoh, T. Itoh, and M. Gomi, IEEE Trans. Magn., **23** (1987) 3432-3434.

Fig. 1 Dependence of internal stress in Ni ferrite films on atomic ratio Ni/Fe in reaction solution for $h=100$ and 130mm .

Fig. 2 X-ray diffraction diagram of Ni ferrite plated films prepared at Ni/Fe of 0.42 and 0.83 at $h=100\text{mm}$.