Preparation of Supersaturated Fe–In Alloy Thin Films by Ion-Plating Process*1

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In this study, Fe–In (Fe–IIIB system) alloys of ferromagnetic thin films supersaturated with indium were prepared by a triode-type ion-plating process with dual vapor sources. The preparation of the supersaturated Fe–In thin films is discussed on the basis of the effect of excess energy on the nanostructure of thin films. The kinetic energy of ions and the ionization rate in evaporation particles were measured using a Langmuir probe and a Faraday cup, respectively. The excess energy of the ion-plating process increased with increasing applied bias voltage of a discharge electrode. X-ray diffraction analysis showed that crystal structures of the supersaturated film samples were α-Fe bcc structures of an iron solid solution alloy. The ion-plating process can control the solubility limit and nanostructure of iron alloy thin films.

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1. Introduction

We previously reported the thin film formation of Fe–IIIB group elements with a body-centered cubic structure and found that aluminum transcended the solid solubility limit in iron by using an ion-plating process.5,6) This indicated that the energy of evaporated particles affected aluminum solubility. We focused on indium, which is a IIIB group element. However, the Fe–In system is immiscible at equilibrium at room temperature.5,6) Thin-film fabrication methods include sputtering,4,5) ion beam-assisted deposition,6,7) and other methods. However, very few studies have reported on the ion plating process. In this study, Fe–In thin films were prepared by an ion-plating process using a dual vapor source, and their properties are discussed in terms of their nanostructure and excess energy during film preparation.

2. Experimental Procedure

2.1 Film preparation

The ion-plating process used in this study is a hybrid vacuum thin-film deposition process combing the benefits of vacuum evaporation and a plasma process. Figure 1 shows a schematic of the ion-plating system with an electron beam evaporation source and resistance heating source. The characteristics of the films prepared by ion plating vary significantly. In this type of ion-plating system, the flux of the source vapor is ionized by accelerated thermal electrons from a molten pool and deposited on an anodic discharge electrode, the so-called “Anode Probe”. We changed the discharge state using the anodic electrode voltage. Table 1 shows the experimental conditions.

2.2 Sample analysis

The compositions of the film samples were measured by energy-dispersive X-ray spectroscopy (EDX). The film nanostructure was determined by X-ray diffraction. The sample thickness was measured using a stylus profilometer.

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2.3 Calculation of excess energy during film preparation

The excess energy of particles in the ion-plating process was defined as the difference between the temperature of the evaporated particles and that of the particles deposited on the substrate. Excess energy during film preparation is given by

\[ E_i = N_A \varepsilon (V_i - V_{sub})i + (3/2)kT_{met} - 3kT_{sub}. \]  

where \( N_A \) [mol\(^{-1}\)] is Avogadro’s constant, \( \varepsilon \) [C] is the elementary charge, \( k \) [J K\(^{-1}\)] is the Boltzmann constant, \( i \) is the ionization rate of the evaporated particles measured using a Faraday cup, \( V_i \) [eV] is the potential of the plasma in the evaporated particles measured using a Langmuir probe, \( V_{sub} \) [V] is the potential of the substrate, \( T_{met} \) is the temperature for the neutral evaporated particles (equal to the temperature of the pool), and \( T_{sub} \) is the temperature of the substrate, which was set to 300–350 K. The ionization rate was estimated on the basis of the ratio between the ions and evaporation particles impinging a unit area of the substrate. In our experiment, we used a Faraday cup as a metal conductive cup to measure ions impinging per unit area. When a packet of ions hits the cup, it conducts a small current while the ions are neutralized. The resulting current can be measured by an ampere meter and then used to determine the number of ions per unit area and per unit time.

3. Results and Discussion

3.1 Ionization rate for evaporated particles

Figure 2 shows the dependence of the ionization rate \( i \) on the applied bias voltage \( V_A \). The ionization rate increased linearly with increasing applied bias voltage. The ionization of evaporated metal was accelerated by an increase in thermal electrons, which was the result of a higher probe voltage. The ionization rates measured in this study are compatible with the reports of other researchers.\(^8\)–\(^10\)

3.2 Effect of excess energy

At the anode probe voltage of +150 V, the ionization rate was about 17% and the plasma potential was about 55 eV measured by a Langmuir probe. Sakudo\(^{11} \) reported that the excess energy in a low-energy ion beam was about 100 eV, which is close to the value of the energy of the evaporated metal particles obtained in this study. \( T_{met} \) was estimated at 3000 K, which is the molten pool temperature, and \( T_{sub} \) was given as 300 K. Substituting these parameters into eq. (1), the calculated \( E_i \) of the ion-plating process was about 0.95 MJ/mol. In a conventional vacuum evaporation process, the value of the excess energy is about 0.03 MJ/mol when the ionization rate and plasma potential are zero. Accordingly, the excess energy in thin film deposition is dominantly provided by the plasma.

3.3 Compound and crystal structure

In the EDX measurement, the composition of the Fe-In alloy thin films were Fe-1.6 at%In, Fe-2.6 at%In, and Fe-9.5 at%In.

As shown in Fig. 3, all samples showed an \( \alpha \)-Fe bcc structure, and the peaks shifted to a lower diffraction angle as the indium concentration increased. These peak shifts were attributed to the substitution of indium into the \( \alpha \)-Fe bcc structure. These results suggest that the Fe-In films exhibit a substitutional solid solution phase. Iron and indium are an immiscible system at room temperature according to the equilibrium diagram of Fe-In. In this work, the Fe-In alloy thin films showed an indium supersaturated solid solution of an iron bcc structure. A supersaturated solid solution thin film formed under the nonequilibrium condition of plasma-solid quenching, unusual for the ion-plating process. Currently, preparation of supersaturated solid solution thin film has been accomplished by applying a large of excess energy via an ion beam mixing method\(^{12,13} \) and ion beam assisted method.\(^{14} \) Ions in the ion beam mixing process have high energy. The ion beam-assisted deposition is accompanied by ion bombardment of an inert gas. Conversely, in the ion-plating process, a deposited thin film is exposed to high-density ion bombardment. It was shown that the supersaturated solid solution can be formed using large excess energy with ion bombardment.

4. Conclusion

In this study, supersaturated Fe-In alloy thin films were prepared successfully by an ion-plating process. The expansion of the solubility limit was due to the vaporized particles ionized in the plasma. Fe-In films with a supersaturated composition can be prepared by controlling the amount of excess energy as a plasma process parameter.
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