

Preparation of Perpendicular GdFeCo Magnetic Thin Films with Pulse Electrodeposition Technique Utilizing Molten Salt as Electrolyte

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We have utilized ZnCl₂-dimethylsulfone (DMSO₂) as the electrolyte with added GdCl₃, FeCl₂, and CoCl₂, for electrodepositing a perpendicular GdFeCo magnetic thin film. The reaction at the electrode surface and the electrical conductivity of the ionic substance at different ionic concentrations were studied by cyclic voltammetry and a computerized direct current method. Moreover, the electrodeposition of the GdFeCo thin film was determined by a pulse potential method. Relation between the composition of the deposited thin film and control parameters including applied potentials was determined by EDS analysis. An amorphous structure and the thickness of the thin film were obtained by TEM analysis. Its roughness and uniformity were determined by AFM analysis. Meanwhile, a perpendicular magnetic property and pinning magnetic domain of the thin film were analyzed from results of AGM and MFM.

Key words: ZnCl₂-DMSO₂ Electrolyte; Perpendicular GdFeCo Magnetic Film; Pulse Potential Method.

1. Introduction

Literature search reveals that perpendicular magnetic materials have been applied to magneto-optical (MO) media [1, 2], recording heads [3, 4], and perpendicular magnetic tunneling junction (pMTJ) [5]. However, preparation of magnetic materials is normally carried out in very expensive high-vacuum systems. Since electrodeposition methods for the preparation of magnetic films have several advantages, such as simple equipment, ease of operation and relatively large area, the use of them has a great potential for preparing magnetic films. Magnetic properties including saturation magnetization (M_s), remanence magnetization (M_r), and coercive field (H_c) form the very important physical basis in ferromagnetic materials. As M_r is nearly equal to M_s , it means that the squareness (M_r/M_s) should approach 1. Consequently, it is shown that the magnetic moment remains fully saturated and the maximum signal of read/write in recording media can be obtained. Electrodeposition of a perpendicular anisotropic magnetic thin film was not an easy operation for an aqueous electrolyte containing rare-earth (RE) and transition metals (TM) in the past. This is

because the rare-earth element has a greater reduction overpotential and has a lower solubility in water. Therefore, the perpendicular anisotropic magnetic thin film containing RE and TM prepared by a molten salt electrolyte would overcome two difficulties as mentioned above. Besides, utilizing sputtering to prepare RE-TM perpendicular magnetic thin films one could obtain a thickness range from 10 to 100 nm [6–8]. Applying an aqueous solution of the electrolyte to produce a perpendicular anisotropic magnetic thin film with transition metals, such as Co/Pt multilayer and single layer films, the squareness could only reach 0.8, and the thickness is about 0.1 to μm [9–11].

2. Experimental

ZnCl₂ (Merck, anhydrous, 98%), DMSO₂ (Acros, 98%), FeCl₂ (Aldrich, anhydrous, 99.99%), CoCl₂ (Merck, anhydrous, 99%), and GdCl₃ (Alfa Aesar, anhydrous, 99.99%) were stored in a glove compartment filled with dry nitrogen gas [12, 13]. Appropriate amounts of ZnCl₂ and DMSO₂ were weighed in a gas-filled compartment. Then, a suitable quantity of ZnCl₂ was slowly added to DMSO₂ while heating be-

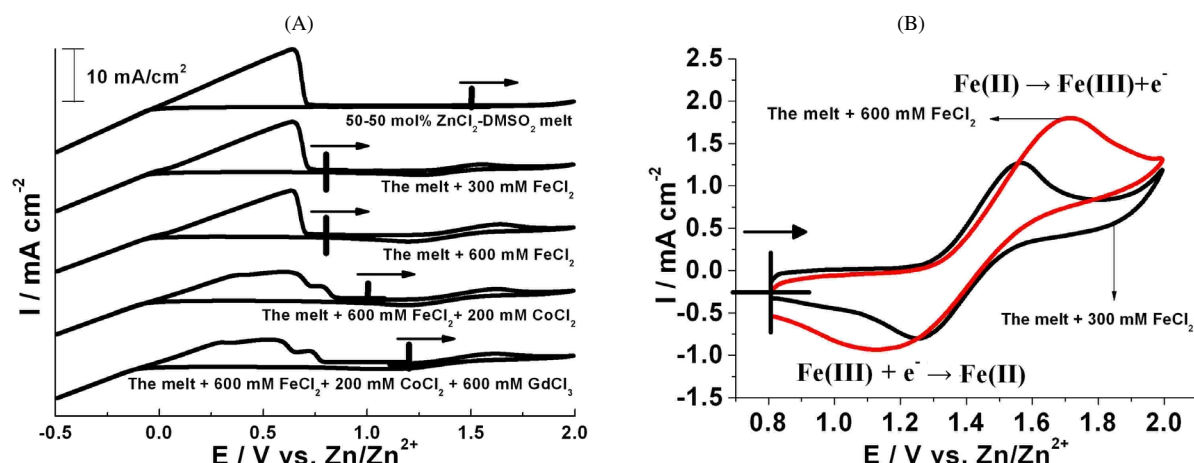


Fig. 1. Cyclic voltammograms recorded on a Pt electrode in 50 : 50 mol% ZnCl_2 -DMSO₂ containing 300 mM FeCl_2 , 600 mM FeCl_2 , 200 mM CoCl_2 , and 600 mM GdCl_3 at 70 °C. (A) Overall curve; (B) minor curve for Fe reaction; scan rate: 100 mV/s.

low 70 °C until the electrolyte became transparent. While maintaining a temperature of 70 °C, different portions of FeCl_2 , CoCl_2 , and GdCl_3 were added to the molten salt until the mixture dissolved completely and gave a semi-transparent appearance.

The electrical conductivity of the molten salt electrolyte mixture for various operating temperatures was determined by a computerized direct current method [12]. A potentiostat/galvanostat instrument (EG & G, Princeton Applied Research, model 273A) was used for electrochemical tests. It was also used for electrodepositing GdFeCo magnetic films on a Pt substrate. In order to increase the adhesion and uniformity of the electrodeposited magnetic films, a sputtered platinum thin film ($\sim 30 \text{ nm}$) on a silicon substrate was used as the deposition plate. An enclosed three-electrode system was used as the electrochemical reactor in this study. Moreover, we used a controlled potentiostat (applied deposition potential, Volt, vs. Zn/Zn^{2+}) to prepare perpendicular magnetic films. Platinum (geometrical area = 0.01767 cm^2 , Nilaco Co., 99.99%) was used as working electrode (WE), and also for investigating the oxidation and reduction of the cation. A $\text{Zn}/[\text{ZnCl}_4]^{2-}$ electrode containing a 50 : 50 mol% ZnCl_2 -DMSO₂ melt in a closed glass tube with an inserted zinc wire (0.8 mm diameter, Nilaco Co., 99.99%) was prepared as reference (geometrical area = 1.25 cm^2) and counter electrodes (geometrical area = 2.5 cm^2). A porous glass frit was used to separate the $[\text{ZnCl}_4]^{2-}$ solution from the molten salt.

The magnetic properties of the magnetic film were analyzed by an alternating gradient magnetometer

(AGM, MicoMagTM 2900), a value of 10 nemurms of high sensitivity could be reached. The system was equipped with a 2-inch laboratory electromagnet. The thickness and crystal structure of the deposited layer were measured by a transmission electron microscope (TEM, Jeol 2010) with an electron diffraction pattern. A scanning probe microscope (SPM, Veeco/DI, D3100) was used to investigate the surface microstructure and magnetic domain of the electrodeposited layer. Moreover, energy dispersive X-ray spectroscopy (EDS, Oxford) was used to identify the film's composition.

3. Results and Discussion

Figure 1A illustrates the cyclic voltammograms of the molten salt electrolyte at different ionic concentrations (300 mM FeCl_2 , 600 mM FeCl_2 , 200 mM CoCl_2 , and 600 mM GdCl_3), while Pt was used as working electrode. One can obviously see an oxidation peak of Zn at 0.62 V. Moreover, the deposition over-potential of Zn metal ranging between -0.5 and -0.1 V , could be observed. No change of the Zn ionic reaction was obtained after adding 300 mM FeCl_2 and 600 mM FeCl_2 . The oxidation and the reduction of one electron on an Fe ion is shown in Figure 1B. The reactions should be $\text{Fe(II)} \rightarrow \text{Fe(III)} + e^-$ and $\text{Fe(III)} + e^- \rightarrow \text{Fe(II)}$. Then CoCl_2 was added to the molten salt. The experimental results revealed that the oxidation peak of Zn has obviously changed from sharp to bluntness, as shown in Fig. 1A with a CoCl_2 concentration of 200 mM. This is proba-

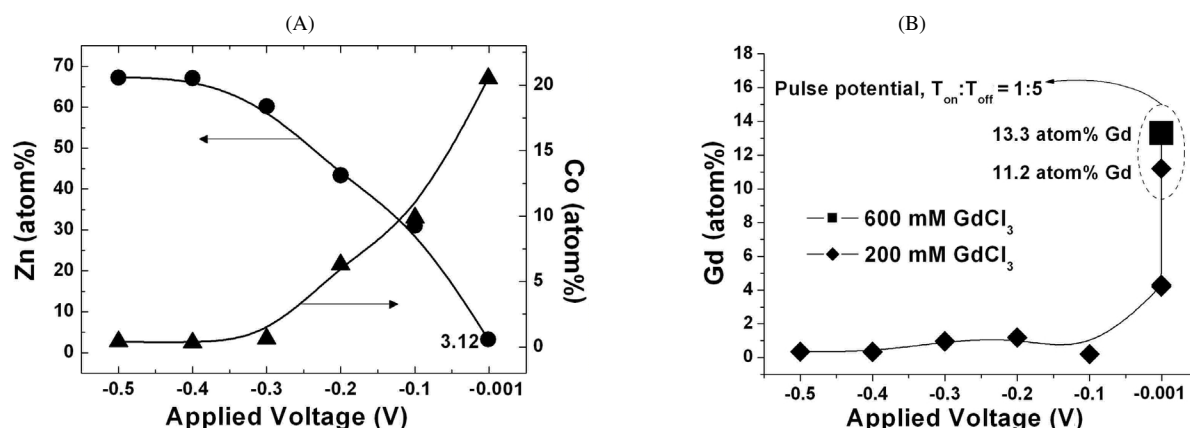


Fig. 2. Relation between layer composition and applied potential for an electrodeposited GdFeCo thin film from 50 : 50 mol% ZnCl₂-DMSO₂ containing 600 mM FeCl₂, 200 mM CoCl₂, 200 mM and 600 mM GdCl₃ at 70 °C. (A) Zn and Co atom%; (B) Gd atom%.

bly due to the reaction between the Co(II) ion and the Zn[(CH₃)₂SO₂]_n²⁺ complex ion resulting in a decreased oxidation-reduction reaction rate of Zn, which is similar to that of the ZnCl₂-DMSO₂-CoCl₂ system [14]. In addition, adding 600 mM GdCl₃ to the mixture for electrodepositing a GdFeCo magnetic thin film did not show a significant change of the electrochemical property of the Gd ions, as shown in Fig. 1A with constructed of 50 : 50 mol% ZnCl₂-DMSO₂-300 mM FeCl₂-600 mM FeCl₂-200 mM CoCl₂-600 mM GdCl₃ melt. The results revealed that the Gd ion in the melt possibly hindered the codeposition reaction with the transition metal ion in the range of the Zn overpotential from -0.5 to -0.1 V. Even though the result was shown in the experiment, the papers [15, 16] had demonstrated the codeposition reaction of rare-earth and transition metals. Hence, the 3d orbital electrons of Fe and Co probably would codeposit with the Gd ion, as it has the 4f5d orbital electron. Based on the above conjecture, we conducted electrodeposition of magnetic thin films and analyzed their layer composition. The relation between the layer compositions (Zn, Co, and Gd) and the applied potentials (-0.001 ~ -0.5 V) are shown in Figs. 2A and 2B. The results revealed that the amount of Zn metal in the deposited layer decreased with the decrease of the applied potential from -0.5 to -0.001 V, and only 3.12 atom% of Zn metal were obtained at -0.001 V, whereas the amount of Co and Gd metal in the deposited layer increased with decreasing applied potential. Besides, when the concentration of GdCl₃ was increased from 200 mM to 600 mM, the increase of the Gd percentage in the

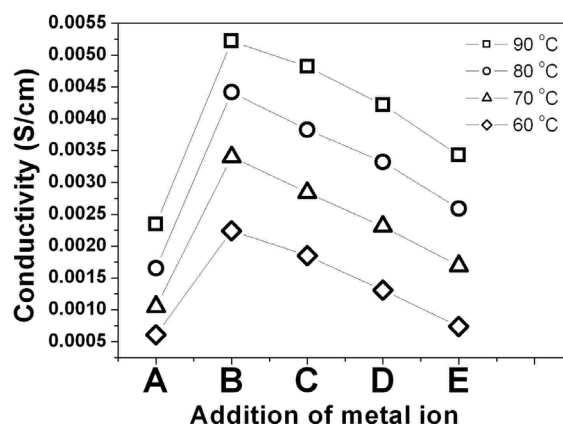


Fig. 3. The isotherms of electrical conductivity as functions of the ionic content in 50 : 50 mol% ZnCl₂-DMSO₂ at 60–90 °C. A, 50 : 50 mol% ZnCl₂-DMSO₂; B, 50 : 50 mol% ZnCl₂-DMSO₂, 600 mM FeCl₂; C, 50 : 50 mol% ZnCl₂-DMSO₂, 600 mM FeCl₂, 200 mM CoCl₂; D, 50 : 50 mol% ZnCl₂-DMSO₂, 600 mM FeCl₂, 200 mM CoCl₂, 200 mM GdCl₃; E, 50 : 50 mol% ZnCl₂-DMSO₂, 600 mM FeCl₂, 200 mM CoCl₂, 600 mM GdCl₃.

deposited layer reached only 2.1 atom%, as shown in Figure 2B. This is probably due to the deterioration of the transport property of the molten salt electrolyte that slowed down the deposition of Gd. The results revealed that Fe and Gd ions could undergo codeposition reactions at low potential. In addition, the deposited layer of GdFeCo containing 13.3 atom% Gd, 57.1 atom% Fe, and 29.6 atom% Co has the maximum Gd amount while applying a voltage of -0.001 V.

Isotherms of the electrical conductivity as function of ionic concentrations (300 mM FeCl₂, 600 mM

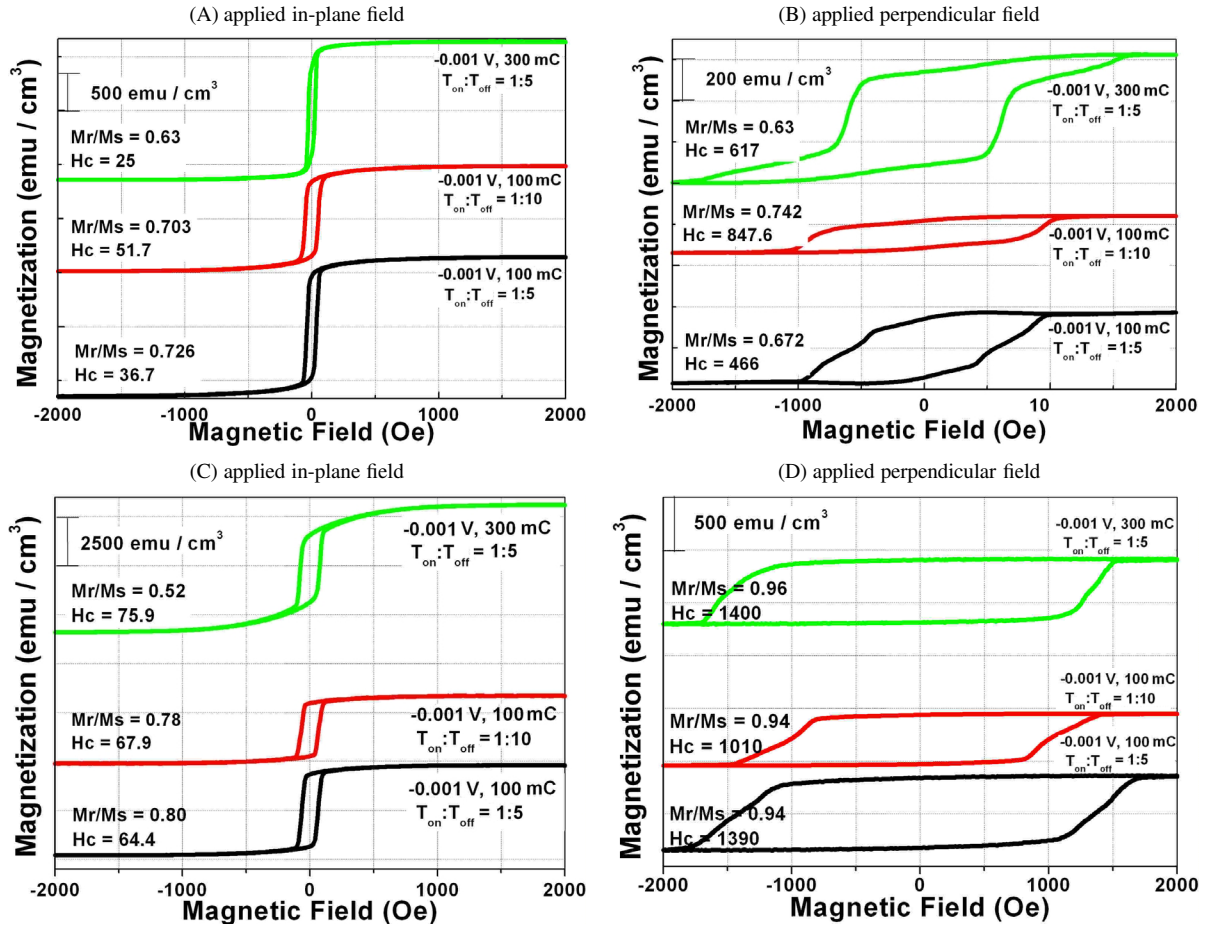


Fig. 4. Hysteresis loops of GdFeCo alloy electrodeposited from a mixture of the 50 : 50 mol% ZnCl_2 -DMSO₂, 600 mM FeCl_2 , 200 mM $\text{CoCl}_{2-x}\text{GdCl}_3$ melt on a Pt/Si plate at 70 °C. (A), (B) $x = 200$ mM; (C), (D) $x = 600$ mM. Experimental conditions: pulse potential mode; $T_{\text{on}}:T_{\text{off}} = 1:5$ and $1:10$; applied voltage -0.001 V; $Q = 100$ and 300 mC.

FeCl_2 , 200 mM CoCl_2 , and 600 mM GdCl_3) in 50 : 50 mol% ZnCl_2 -DMSO₂ at 60–90 °C are shown in Figure 3. The results revealed that the electrical conductivity of the molten salt electrolyte increased when 600 mM FeCl_2 was added to the 50 : 50 mol% ZnCl_2 -DMSO₂ molten salt. However, the electrical conductivity decreased in the mixture in the B to E melts. This is because the electrical conductivity, κ , reflects the overall ionic mobility and can be expressed as: $\kappa = F \sum Z_i u_i C_i$, where F is the Faraday constant and u_i is the ionic mobility of the i -th species. Therefore the electrical conductivity increased with increasing ionic amount. However, too many metal ions in the ZnCl_2 -DMSO₂ system would result in increased interactions and higher viscosity of the system. This will decrease the conductivity. Increased conductiv-

ity was seen when 600 mM FeCl_2 was added, which increased the ion concentration. However, subsequent addition of chlorides resulted in decreased conductivity. The transport property depends on the formation and stability of complex species. In the molten ZnCl_2 -DMSO₂ system [12], the conductivity of 40–70 mol% ZnCl_2 molten compositions was measured in the range from $1.17 \cdot 10^{-3}$ to $1.93 \cdot 10^{-4}$ S/cm at 60 °C, its thermal stability range of liquid state was determined from -56.54 to 205.38 °C. We found that a higher conductivity and more thermal stability of the composition at 50 mol% ZnCl_2 were obtained. Hence, 50 mol% ZnCl_2 was utilized as molten salt in this work. Moreover, the $[\text{ZnCl}_4]^{2-}$ and $\text{Zn}[(\text{CH}_3)_2\text{SO}_2]_n^{2+}$ complex ions of 50 mol% ZnCl_2 were consumed by the addition of Co, Fe, and Gd ions and the formed com-

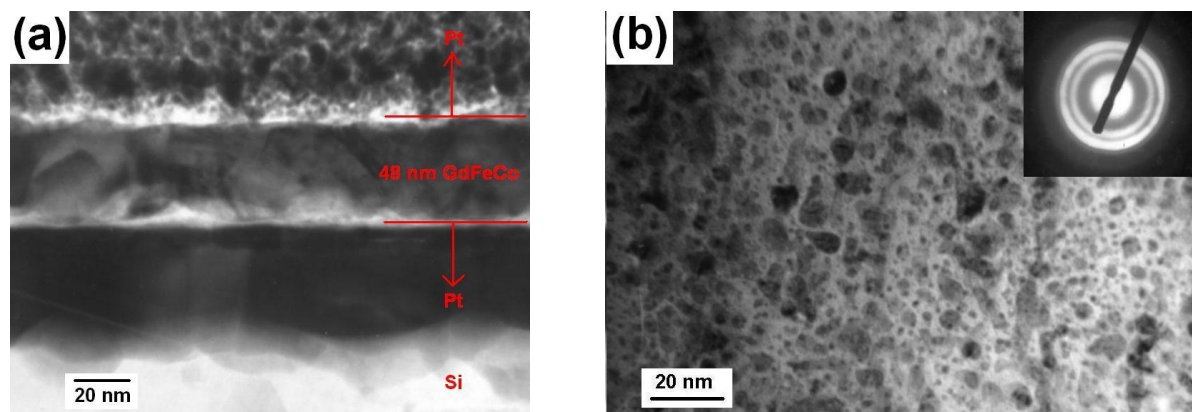


Fig. 5. TEM images of a GdFeCo thin film electrodeposited on a Pt/Si plate at 70 °C from a mixture of 50 : 50 mol% ZnCl_2 - DMSO_2 , 600 mM FeCl_2 , 200 mM CoCl_2 , 600 mM GdCl_3 . (a) Section view; (b) plane view. Experimental conditions: applied deposition potential -0.001 V, pulse potential mode; $T_{\text{on}} : T_{\text{off}} = 1 : 5$; $Q = 100$ mC. The inserted image of a plane view is a diffraction pattern.

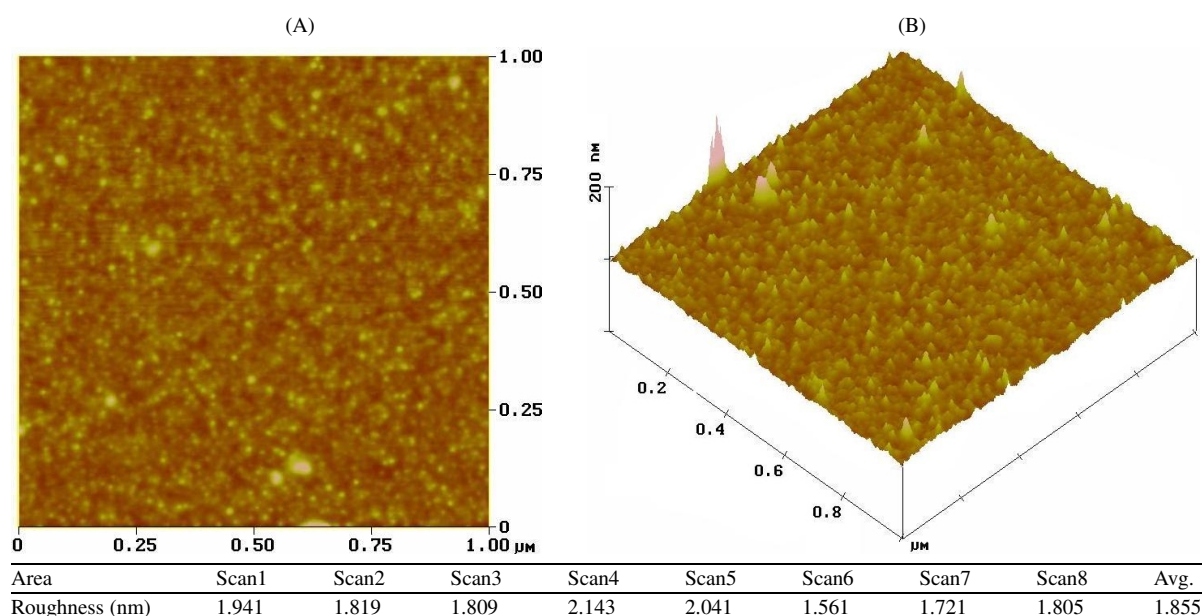


Fig. 6. AFM images of a GdFeCo thin film electrodeposited on a Pt/Si plate at 70 °C from a mixture of 50 : 50 mol% ZnCl_2 - DMSO_2 , 600 mM FeCl_2 , 200 mM CoCl_2 , 600 mM GdCl_3 . Experimental conditions: pulse potential mode; $T_{\text{on}} : T_{\text{off}} = 1 : 5$; applied deposition potential -0.001 V; $Q = 100$ mC. (A) 2-D; (B) 3-D.

plex species contained larger ions, $[\text{MCl}_4]^{m-}$ and $\text{M}[(\text{CH}_3)_2\text{SO}_2]_n^{m+}$ ($\text{M} = \text{Gd}, \text{Fe}, \text{and Co}$). These complex ions show lower mobility than the smaller ions $[\text{ZnCl}_4]^{2-}$ and $\text{Zn}[(\text{CH}_3)_2\text{SO}_2]_n^{2+}$. Therefore, the electric conductivity decreased after addition of more metal ions.

Hysteresis loops of the GdFeCo magnetic films made under controlled conditions such as applied deposition potential of -0.001 V, pulsation ratio $T_{\text{on}} : T_{\text{off}}$

of 1 : 5 and 1 : 10, and electrical quantity of 100 and 300 mC in a molten salt electrolyte containing 200 mM GdCl_3 are shown in Figs. 4A and 4B. The saturation magnetization (M_s), coercive field (H_c), and squareness (M_r/M_s) were measured and are shown in the insets. Results revealed that a squareness of $0.63 \sim 0.74$ and H_c of $460 \sim 850$ Oe were obtained from the analyzed results of hysteresis loops with a perpendicular field. Moreover, we selected an electrolyte con-

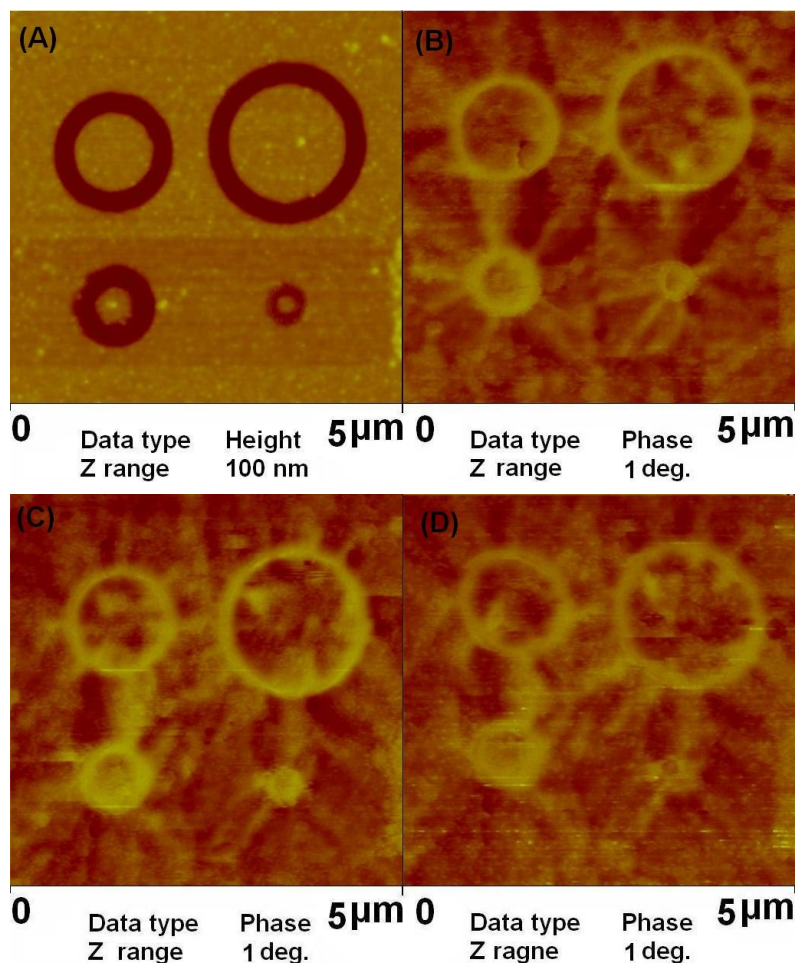


Fig. 7. Atomic and magnetic force micrographs of a GdFeCo thin film electrodeposited on a Pt/Si plate at 70 °C from a mixture of 50:50 mol% ZnCl_2 -DMSO₂, 600 mM FeCl_2 , 200 mM CoCl_2 , 600 mM GdCl_3 . Experimental conditions: pulse potential mode; $T_{\text{on}}:T_{\text{off}} = 1:5$; applied deposition potential -0.001 V; $Q = 100$ mC. (A) AFM; (B) MFM at 0 Oe; (C) MFM at +10 kOe; and (D) MFM at -10 kOe.

taining 600 mM GdCl_3 for electrodepositing a GdFeCo magnetic thin film. A high squareness of $0.94 \sim 0.96$ and H_c of $1000 \sim 1400$ Oe could be obtained, as shown in Figs. 4C and 4D. It is probably due to the Gd amount of the deposited layer in the electrolyte containing 600 mM GdCl_3 higher than in the former. This reason is shown in Figure 2B. Their magnetic properties are approached results from sputtering [15]. A comparison of the results of magnetic properties of a perpendicular and in-plane field is shown in Figs. 4A and 4B. It can be seen that both the squareness and H_c of the perpendicular field are higher than that those of an in-plane field.

Figure 5 shows cross-section, morphology and diffraction pattern of the GdFeCo magnetic film with the pulse potential mode at -0.001 V. We can see that a good deposition layer is obtained, and the thin film's thickness of 48 nm could be measured through TEM

analyses. Moreover, the electrodeposited GdFeCo thin film prepared by the pulse potential mode showed a structure of fine and smooth layers. The thickness of RE-TM thin films was compared with that of the sputtering method. The thin film prepared by sputtering had a thickness of about $30 \sim 35$ nm and was used for application to magnetic-optic materials [17–20]. In addition, an amorphous structure prepared by the pulse potential mode using the molten salt electrodeposition method was obtained from TEM diffraction. In [21], an amorphous structure of the TbFeCo multilayer thin film prepared by the sputtering system was also reported. It had similar results as shown in the diffraction pattern of Figure 5b.

Atomic force micrographs of a GdFeCo thin film prepared by a controlled potential of -0.001 V and at a pulsed ratio of $T_{\text{on}}:T_{\text{off}}$ of $1:5$ are shown in Figure 6. The surface of the deposited layer obtained by apply-

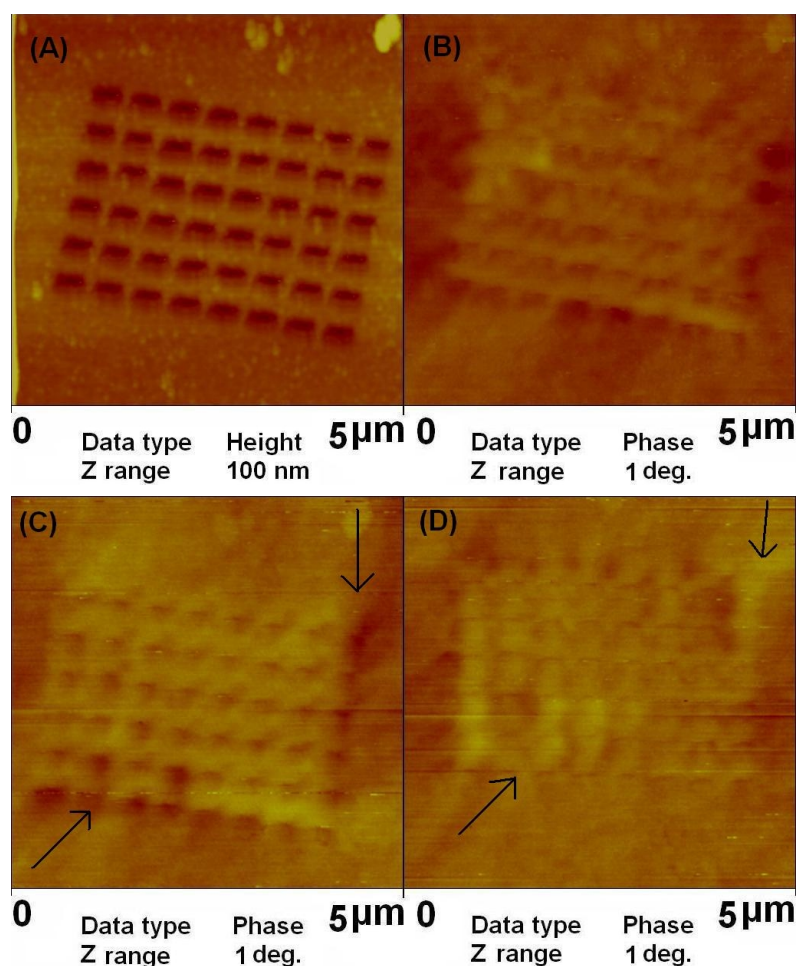


Fig. 8. Atomic and magnetic force micrographs of a GdFeCo thin film electrodeposited on a Pt/Si plate at 70 °C from a mixture of 50:50 mol% ZnCl_2 -DMSO₂, 600 mM FeCl_2 , 200 mM CoCl_2 , 600 mM GdCl_3 . Experimental conditions: pulse potential mode; $T_{\text{on}}:T_{\text{off}} = 1:5$; applied deposition potential -0.001 V; $Q = 100$ mC. (A) AFM; (B) MFM at 0 Oe; (C) MFM at +10 kOe; and (D) MFM at -10 kOe.

ing -0.001 V showed a structure of tightly packed granular crystals. Moreover, a diameter of $4 \sim 7$ nm was obtained. The table of Fig. 6 shows the average of mean roughness to be 1.855 nm (analyzed eight points in the $1 \cdot 3$ cm area). It is clear that the deposition layer of the GdFeCo thin film obtained by the molten salt electrodeposition method has superior smoothness. The surface structure of the Co-Zn magnetic film was observed by -0.1 and -0.5 V from the molten ZnCl_2 -DMSO₂- CoCl_2 system [14], revealing that the grain size and roughness of the GdFeCo thin film were lower than that of Co-Zn. On the other hand, a GdFeCo thin film with a roughness of ~ 0.369 nm, prepared by sputtering in our lab, was much lower than that obtained by the electrodeposition method.

The surface morphology of the GdFeCo thin film observed using an atomic force microscope (AFM) is shown in Figure 7A. The pattern size and depth were

measured by section analyses. The constructed patterns were: 1) 52 nm internal diameter (Di) with a depth of 28 nm; 2) 527 nm Di with a depth of 320 nm; 3) 957 nm Di with a depth of 320 nm; and 4) 1440 nm Di with a depth of 2320 nm. The analysis using a magnetic force microscope (MFM) after carrying out the demagnetization process when applying magnetic fields of ± 10 kOe is shown in Figure 7B. It is clear that the magnetic domain at the pattern area revealed the pinning effect. Therefore, the magnetic moment was carried out parallel to each other on repulsion. Moreover, results obtained by applying a magnetic field of 10 kOe and -10 kOe to the GdFeCo film are shown in Figs. 7C and 7D, respectively. No saturated magnetic moment at the circle area was observed from pattern 2 to pattern 4, whereas the circle area in pattern 1 was saturated from lower patterned depth. A pattern depth approach of ~ 50 nm utilizing magnetic-

optic thin film has been reported in several papers [17–20]. Furthermore, we have also changed the pattern size and depth by forming a rectangular array structure with a dimension of 352 nm H · 176 nm W · 46 nm D as shown in Figure 8A. A random structure of magnetic domain was obtained after demagnetization, as shown in Figure 8B. The magnetization observed in each magnetic domain obtained by the interaction of the magnetic moments of atoms is a consequence of the magnetic physics, so that spin up is equal to its corresponding spin down. Moreover, the magnetic spin down and spin up of pattern arrays are shown in Figs. 8C and 8D when applying magnetic fields of 10 kOe and –10 kOe, respectively. A more obvious magnetic force was shown in the indicated arrow of Figure 8. The results revealed that the interaction of two spin electrons formed from the magnetic pole depended on the applied magnetic field; therefore, continuity and uniformity of magnetic reversal structure could be observed for different directions of the magnetic field. Besides, a reverse of magnetic domain was influenced by changing the direction of the magnetic field and by the depth of the pinning pattern. Hence, the magnetizable magnetic moment and the magnetic domain stability are closely related to the

magnetic properties, such as squareness (M_r/M_s) and coercive force (H_c).

4. Conclusion

In summary, we have successfully prepared a perpendicular magnetic film by a molten ZnCl_2 -DMSO₂ electrolyte using the electrodeposition technique. A high squareness ($M_r/M_s = 0.96$) and coercive force ($H_c = 1400$ Oe) of magnetic properties were observed for a perpendicular GdFeCo magnetic thin film deposited at –0.001 V and $T_{\text{on}} : T_{\text{off}} = 1 : 5$ in a 50 : 50 mol% ZnCl_2 -DMSO₂-600 mM FeCl_2 -200 mM CoCl_2 -600 mM GdCl_3 electrolyte at 70 °C. Moreover, a uniform surface and amorphous structure of the deposited layer was obtained while applying a voltage of –0.001 V, which had a pulse ratio ($T_{\text{on}} : T_{\text{off}}$) of 1 : 5 and 1 : 10. From the results of MFM analyses, the reverse of the magnetic domain on a GdFeCo magnetic thin film patterned by a pinning array could be observed after applying a perpendicular field.

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