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# Role of electrolyte pH on structural and magnetic properties of Co–Fe films

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ABSTRACT

Co–Fe films were electrodeposited on polycrystalline Titanium substrates from the electrolytes with different pH levels. X-ray diffraction (XRD) was used to study the crystal structure of the films. The XRD patterns showed that the films grown at the pH levels of 3.70 and 3.30 have a mixed phase consisting of face-centred cubic (fcc) and body-centred cubic, while those grown at pH=2.90 have only fcc structure. It was observed that the film composition, by energy dispersive x-ray spectroscopy, contain around 88 at% Co and 12 at% Fe for all films investigated in this study. Morphological observations indicated that all films have grainy structure with the slight change of grain size depending on the electrolyte pH. Magnetoresistance measurements, made at room temperature, showed that all films exhibited anisotropic magnetoresistance, which is affected by the electrolyte pH. From the magnetic measurements made by vibrating sample magnetometer, the saturation magnetization increases as the electrolyte pH decreases. Furthermore, all films have in-plane easy-axis direction of magnetization.


## 1. Introduction

Magnetic films have attracted much attention due to their potential applications in computer read/write heads. Single ferromagnetic films of transition metals such as Ni, Fe Co and their alloys exhibit anisotropic magnetoresistance (AMR) [1,2].

The most common film growth processes such as sputtering and molecular beam epitaxy (MBE) require high or ultrahigh vacuum. It is also possible to grow such ferromagnetic films with high quality by electrodeposition, which does not need any vacuum system. Moreover, it has more advantages like low cost, fast production and deposition of large areas. In electrodeposition, the growth mechanism, morphology and microstructural properties of the films depend on electrodeposition conditions such as electrolyte pH, deposition potential and electrolyte composition. The electrolyte pH was observed to change significantly the microstructure, morphology and magnetotransport properties of electrodeposited films [3].

In this study, the structural, magnetic and magnetoresistance properties of electrodeposited Co–Fe films were investigated as a function of the electrolyte pH. It was observed that the crystal structure was changed significantly with the electrolyte pH while the AMR value was slightly affected by it.

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## 2. Experimental

In this study, Co–Fe films were grown from an electrolyte containing $Co^{+2}$ and $Fe^{+2}$ ions under the potentiostatic conditions. Electrodeposition was performed in an electrochemical cell with three electrodes using a potentiostat/galvanostat (EGG Model 362). The electrolyte was composed of 0.5 M cobalt sulphate, 0.1 M iron sulphate, and 0.3 M boric acid. All chemicals were reagent grade and dissolved in distilled water. A platinum (Pt) sheet with an area of 6 $cm^2$ was used as counter electrode. The reference electrode was a saturated calomel electrode (SCE). Titanium (Ti) sheet was served as a substrate. Prior to deposition, the substrate was first mechanically polished, then washed in 10% $H_2SO_4$ and distilled water.

Co–Fe films were deposited at a cathode potential of –2.5 V vs. SCE. The charge amount required for the film thickness was calculated in according to the Faraday law by assuming 100% current efficiency and the nominal thickness of all films was fixed at 3 μm. However, the true value of current efficiency is less than 100% due to the hydrogen evolution at the cathode. The current efficiency was found to be 86% using the ratio of the measured mass to the nominal mass of the deposits. This means that the real thickness of the deposits corresponds to ~2.6 μm. In order to study the pH effect, the pH was settled down to the desired value by the metal deposition using an inert anode. The change of ion concentration caused by this process is insignificant.

The crystal structure of the films was studied using X-ray diffraction (XRD) technique. The composition analysis was carried out by energy dispersive X-ray spectroscopy (EDX). Scanning electron microscope (SEM) was used to study the surface morphology of the films. Magnetoresistance measurements were made at room temperature in the magnetic field range of $\pm 10$ kOe using van der Pauw method with four point probes arranged in a square. Magnetic properties of the films were investigated using a vibrating sample magnetometer (VSM).

## 3. Results and discussion

The crystal structure of Co–Fe films deposited at three different pH values (3.70, 3.30 and 2.90) was analysed and the XRD patterns were given in Fig. 1. As seen from Fig. 1(a) and (b), the reflections from characteristics {1 1 1}, {2 0 0}, {2 2 0} and {3 1 1} crystal planes of the face-centred cubic (fcc) structure were seen at approximately $2\theta$=44°, 52°, 76° and 91°, respectively. Besides, the {1 1 0} and {2 0 0} peaks of body-centred cubic (bcc) structure were observed at $45^0$ and $65^0$, respectively. The patterns indicate that the films grown at pH=3.70 and pH=3.30 have a mixed phase of fcc and bcc but the fcc phase is dominant. As the pH decreases, bcc/fcc ratio decreases and the {1 1 0} and {2 0 0} peaks of bcc disappear at pH=2.90. The structure becomes completely fcc as seen in Fig. 1(c). This may be attributed to adoption of fcc Co at low pH levels. Thus, the structure of the sample significantly depends on the electrolyte pH.

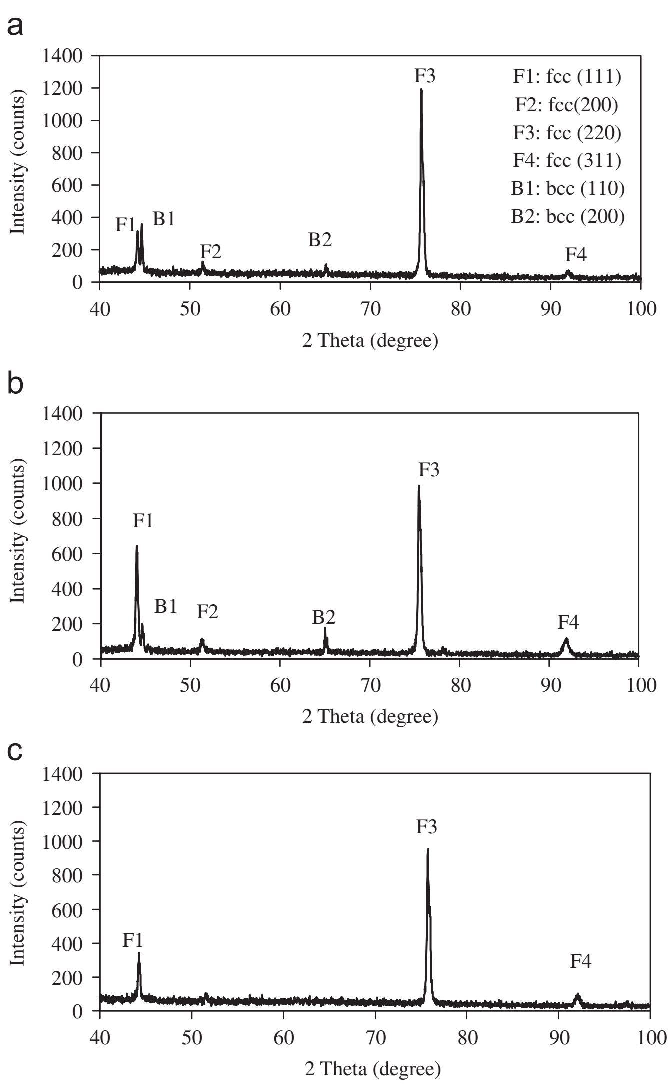


**Fig. 1.** XRD patterns of Co–Fe films grown at pH=3.70 (a), pH=3.30 (b), pH=2.90 (c) (F1:fcc (111), F2:fcc (200), F3:fcc (220), F4:fcc (311), B1:bcc (110), B2:bcc (200)).

Using the least squares method, the average value of lattice parameters were determined to be $(0.3553 \pm 0.0132)$ nm for fcc phase and $(0.2862 \pm 0.0065)$ nm for bcc phase, which are in agreement with the values reported in [4].

According to the EDX results, all films produced in this study contain approximately 88 at% Co and 12 at% Fe. Compositional analysis results are presented in Table 1. Fig. 2(a) and (b) show the SEM micrographs of the films deposited at pH=3.70 and pH=2.90, respectively. The morphological investigation indicated that all films have similar grainy structure, however, when the films are prepared at high pH (3.70), they have larger grains compared to those prepared at low pH (2.90). The change of grain size may be explained by the hydrogen evolution, which is favoured at low pH. Recent studies [5,6] showed that deposition parameters, for example pH, affect the microstructure of electrodeposited metal films.

The percentage changes in the van der Pauw (VDP) resistance, % change in magnetoresistance, labelled as MR (%), as a function of the applied magnetic field, were calculated according to the relation MR (%)=$\{[R(H)-R_{\min}]/R_{\min}\}\times 100$, where R(H) is the value of the resistance at any magnetic field and $R_{\min}$ is the value at the field where the resistance is minimum. As an example, the magnetoresistance curves, the longitudinal magnetoresistance, LMR (triangle), and the transverse magnetoresistance, TMR (circle) of a Co–Fe film are given in Fig. 3. The LMR and TMR values are on average 4.5 and 3.0, respectively, for the films grown at different pH values. As seen from the figure, as the magnetic field increases, LMR increases while TMR decreases. The behaviour observed in the AMR is similar to those observed in ferromagnetic materials such as Ni, Co, Ni–Co [7]. Although the electrolyte pH affects the crystal structure, it does not have a considerable effect on AMR.

Hysteresis loops were measured to obtain the magnetic properties of the films at room temperature. The data obtained from the loops was presented in Table 1. The saturation magnetization increases from 1351 to 1597 emu/cm$^3$ as the electrolyte pH decreases from 3.70 to 2.90, and the coercivity of the films varies between 26–31 Oe. As an example, in-plane and perpendicular hysteresis loops of Co–Fe film deposited at pH=2.90 were shown in Fig. 4. The in-plane hysteresis loop has a higher remenant magnetization and lower coercivity than the perpendicular loop. This indicates that the easy-axis direction of the magnetization is parallel to the film plane. As a result of demagnetizing effect, the shape anisotropy dictates the film must have planar easy axis. The planar magnetization loops were observed for all films.

## 4. Conclusions

Co–Fe films were electrodeposited on Titanium substrate at different pH levels. The crystal structure of Co–Fe films are significantly affected by the electrolyte pH. The films grown at high pH levels (3.70 and 3.30) have a mixed phase (fcc+bcc), but at low pH (2.90) they show only fcc phase. According to the compositional analysis, all films contain around 88 at% Co and 12 at% Fe, irrespective of electrolyte pH. The morphological investigation indicated that films have grainy structure, however, the films grown at high pH (3.70) have larger grains compared to those prepared at low pH (2.90). All films investigated in this study exhibited anisotropic magnetoresistance (AMR), but a considerable change in their AMR values was not detected. The

**Table 1**
Results of microstructural and magnetic measurements of Co–Fe films.

| Electrolyte pH | Structural analysis | | | | | | Magnetic analysis | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Composition analysis (EDX) | | Crystal structure (XRD) | | Lattice parameter (nm) | | Magnetoresistance measurements | | Magnetic measurements (VSM) | |
| | at% Co | at% Fe | fcc (%) | bcc (%) | fcc | bcc | LMR | TMR | $H_c$ (Oe) | $M_s$ (emu/cm$^3$) |
| 3.70 | 88.5 | 11.5 | 82 | 18 | 0.3556 | 0.2862 | 4.4 | 2.7 | 29 | 1351 |
| 3.30 | | | 87 | 13 | 0.3555 | 0.2862 | 4.7 | 3.0 | 31 | 1516 |
| 2.90 | 88.0 | 12.0 | 100 | – | 0.3550 | – | 5.2 | 3.6 | 26 | 1597 |

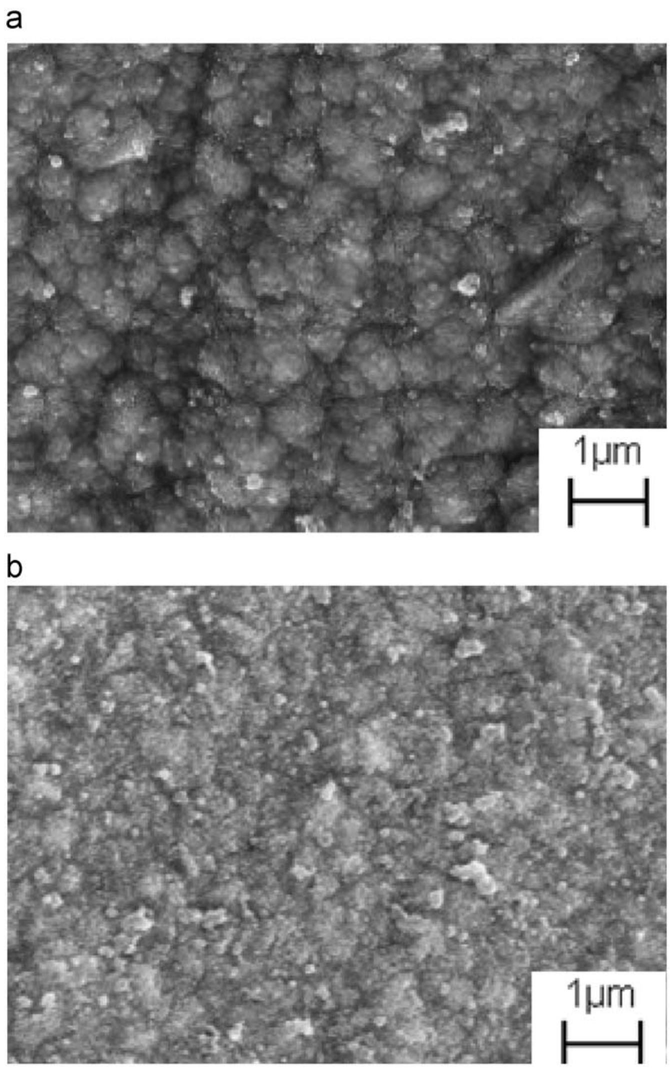


**Fig.2.** SEM images of Co–Fe films deposited at (a) pH=3.70, (b) pH=2.90.

magnetic properties are observed to vary depending on the electrolyte pH and also all films have planar magnetization.

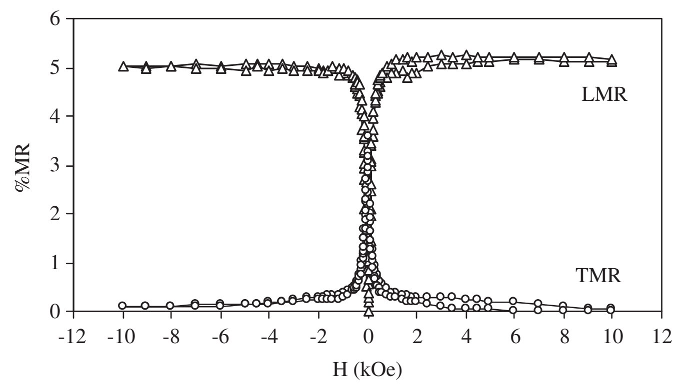


**Fig. 3.** MR curves of Co–Fe films deposited at pH=2.9.

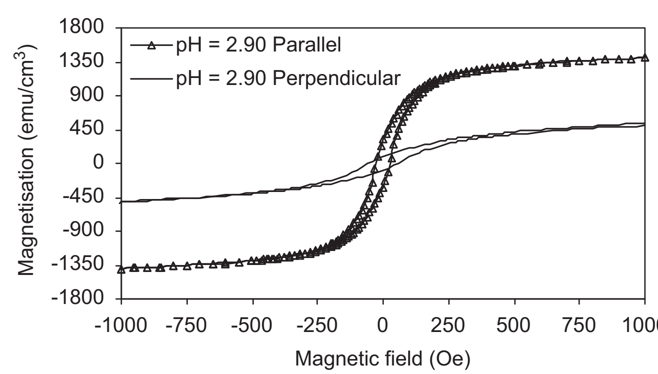


**Fig. 4.** In-plane and perpendicular hysteresis loops of Co–Fe films.

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