Structural, magnetotransport and magnetic properties of the electrodeposited Ni-Fe films arising from electrolyte pH

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Ni-Fe films were grown on polycrystalline titanium substrates by electrodeposition. Microstructure, magnetoresistance and magnetic properties of the films were studied as a function of the electrolyte pH. Structural characterizations by X-ray diffraction showed that all films have face centred cubic structure, but the crystal texture degree was different for the films grown at high and low pH levels. At low pH the films have a preferred (111) orientation, at high pH preferred orientation is the (220). The compositional analysis revealed that the Fe content of the films increases as the electrolyte pH decrease. It was found that all films exhibited anisotropic magnetoresistance (AMR). The AMR values of the films grown at high pH are larger compared to the films at low pH. It was observed that the saturation magnetisation increases due to the increase of the Fe content in the films and the coercivities are almost constant. The magnetic easy axis is in the film plane for all samples. The differences observed in the magnetic and magnetotransport properties of the films most probably arise from the structural and compositional changes caused by the electrolyte pH.

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1. Introduction

The nickel-iron deposits have been of considerable interest for magnetic devices such as recording media and magnetoresistive sensors because of having excellent magnetic properties [1]. Single ferromagnetic films such as Ni, Fe, Co and their alloys exhibit anisotropic magnetoresistance (AMR) [2, 3]. The AMR effect has been widely studied since it was discovered by Thomson in ferromagnetic materials [4]. The effect is a relative change in resistivity between the fully magnetised and demagnetised states [5]. Most of alloys are usually produced by electrodeposition as well as vacuum systems such as sputtering and molecular beam epitaxy. Electrodeposition technique is especially interesting due to its low cost and high quality of the deposits, being extensively used to fabricate the metallic films [6,7]. The properties of the electrodeposited films are significantly affected by parameters such as the electrolyte concentration, the electrolyte pH, the deposition potentials, additives and deposition type. Among these, the electrolyte pH has a significant effect on several factors such as crystalline structure, deposit morphology and current efficiency [8]. Thus, the purpose of the present study is to investigate the structural, magnetotransport and magnetic properties of the Ni–Fe films grown on titanium (Ti) substrate at different pH levels. It was observed that the structural and magnetic properties of the films are considerably affected by the electrolyte pH.

2. Experimental

The Ni-Fe films were electrodeposited from an electrolyte composed by 0.5 M nickel sulphate, 0.1 M iron sulphate and 0.2 M boric acid. After the addition of all chemicals the electrolyte pH was 3.1 and its pH value was lowered to desired values in steps by passing current through it. The current leads to the reduction of metal ions at the cathode and their replacement by hydrogen ions, lowering the electrolyte pH to the desired values [8]. Polycrystalline Ti sheets with a geometric area of 2.9 cm^2 were used as substrate and one face of each substrate was polished mechanically using emery papers of successively increasing grades, and covered with electroplating tape, except for deposition area. The uncovered area was washed in 10 % sulphuric acid and distilled water respectively. The deposition was carried out in a three electrode cell using a potentiostat /galvanostat (EGG Model 362) controlled by a computer potentiostatically. The anode was a platinum foil and saturated calomel electrode (SCE) served as the reference electrode. The films were deposited at -1.5 V with respect to the SCE at room temperature from unstirred aqueous solution. The nominal thickness of the deposits was fixed at 3 µm. After the deposition is completed, the films were mechanically peeled of their substrates and mounted on glass foil.

The crystal structure of the deposits was determined by X-ray diffraction (XRD) with Cu K_α radiation (0.15406 nm). For a general pattern the range recorded was 2θ = 40º–100º with step size 0.02º. The composition of films was measured by energy dispersive X-ray (EDX) spectrometry in the SEM and comparative measurements were also made using inductively coupled plasma atomic emission spectrometry (ICP-AES). Magnetoresistance (MR) measurements were carried out at room temperature using the Van der Pauw (VDP) geometry with four point probes arranged in a square (area 1 cm^2) [9]. The magnetic field applied in the film plane was changed up to ±10 kOe. Magnetic characteristics of the films were investigated with a vibrating sample magnetometer (VSM; ADE EV9 model) at room temperature. A magnetic field up to ±15 kOe was applied both parallel and perpendicular to the plane of the films.

3. Results and discussion

In order to investigate the pH effect on the crystalline structure and texture of Ni-Fe films, X-ray diffraction patterns of films grown from electrolyte with different pH levels are obtained and shown in Fig. 1. As seen from the XRD patterns, the reflections from the characteristic crystal planes, {111}, {200}, {220} and {311} of the face centred cubic (fcc) structure are seen at 2θ≅44°, 51°, 76° and 93° respectively. The data obtained from the XRD analyses are summarized in Table 1. The lattice parameters were found to be 0.3542±0.0015 nm, 0.3539±0.0016 nm and 0.3536±0.0015 nm for the samples prepared at pH=3.1, 2.5 and 2.0, respectively using the least squares technique to fit experimental data a straight line [10]. The errors in the lattice parameters are the standard errors, which were determined from the standard deviations from the slope. The lattice parameters of the deposits grown at different pH levels are almost the same and also near to the lattice parameter of the Ni. This probably arises from the more Ni content than the Fe in the samples, see EDX and ICP-AES data in Table1. The average grain sizes of the crystallites were obtained by using the Sherrer's method [6]. The average grain sizes of the samples were found to be in the range of 15-20 nm.

To assess the texture formation of films, the relative peak intensities of the observed reflections were considered. These peak intensities are listed in Table 1. The strongest peak in the pattern of the sample grown at high pH is the (220) reflection, in addition to this as the electrolyte pH decreases, the (220) peak intensity weakens and (111) peak becomes preferred. This indicates that the texture formation of the electrodeposited Ni-Fe films affected by the electrolyte pH. All samples have reflection of fcc phase but no reflection of Fe in bcc structure was observed. It has been reported that the electrodeposited Ni-Fe films having such low Fe contents crystallize fcc structure [11-14]. In this study, this most likely occurs because of the low Fe content in the films.

The compositional analyses of the deposits obtained from the EDX spectrometer in the SEM and also from the ICP-AES are listed in Table 1. As seen in Table 1, the results obtained from the two techniques are consistent with each other. The measurements indicate that the Fe content of the films increases as the electrolyte pH decreases.

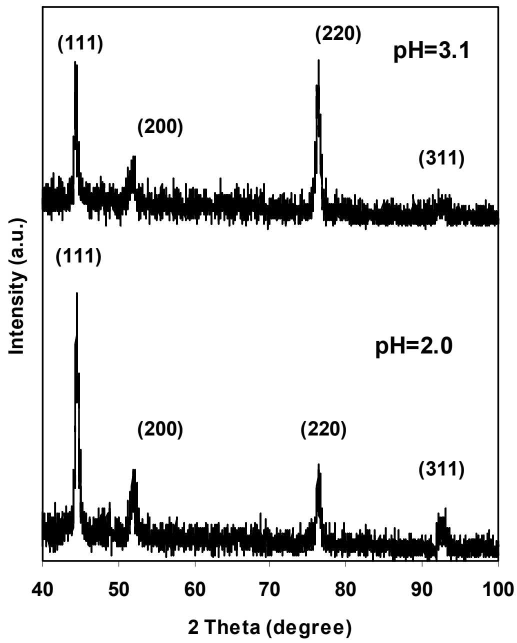

Fig. 1. XRD patterns of Ni-Fe films grown at pH = 3.1 and pH = 2.0

Magnetoresistance measurements of the films from the electrolytes with different pH levels are shown in Fig. 2. The field was applied both parallel and perpendicular to the current flowing in the film plane to measure the longitudinal (LMR) and transverse magnetoresistance (TMR), respectively. The percentage change of the MR(%) as a function of the magnetic field was calculated by equation MR(%)={[R(H)–R_{min}]/R_{min}}x100, where R(H) is the value of resistance at any magnetic field H, and R_{min} is the value at the field where the resistance is minimum.

Ni-Fe films produced at both high and low pH levels exhibited anisotropic magnetoresistance (AMR). In Fig. 2, as the magnetic field increases the LMR increases, while the TMR decreases. The LMR and TMR values are (~5.2 %) (~3.7 %) (~2.4 %), and for the samples grown at pH=3.1, 2.5 and 2.0 levels, respectively. As seen in Fig. 2 the AMR magnitude of the samples decreases with the electrolyte pH. It has been reported that different crystal orientations give the different contribution to the AMR [15].These results may be ascribed to the differences in the texture degrees or the difference in the Fe and Ni content of the films by the electrolyte pH.

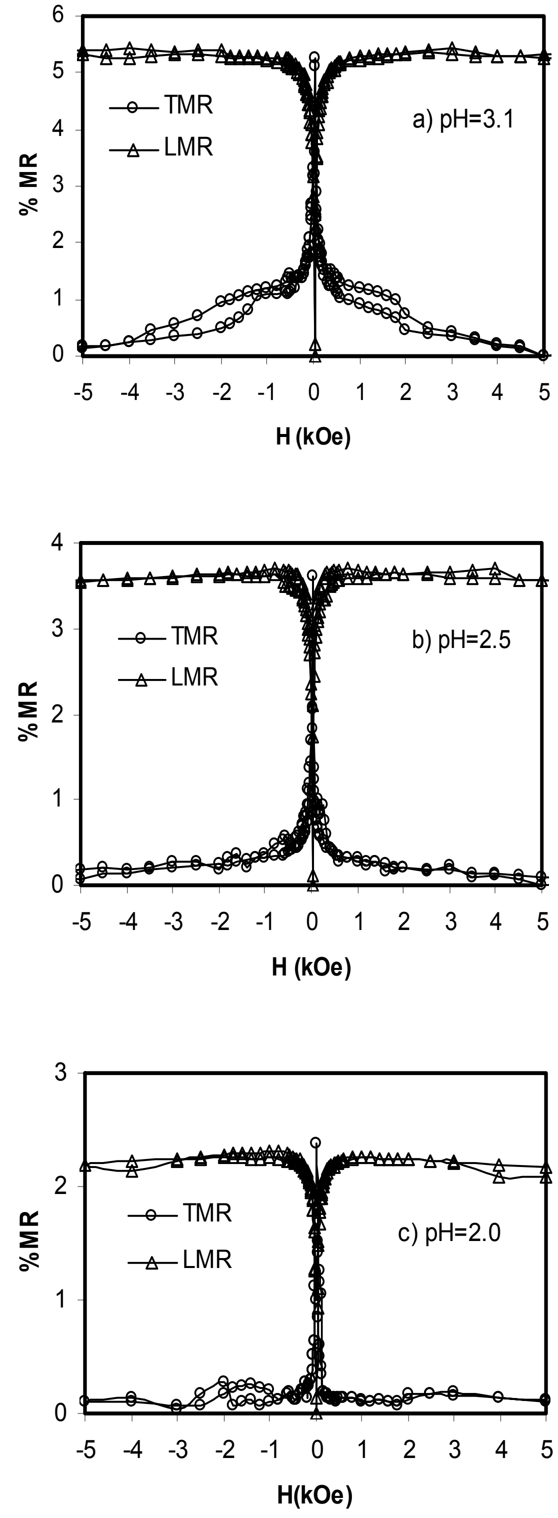

Fig. 2. Longitudinal and transverse magnetoresistance (LMR and TMR) curves of NiFe films grown at a) pH=3.1 b) pH=2.5 c) pH=2.0

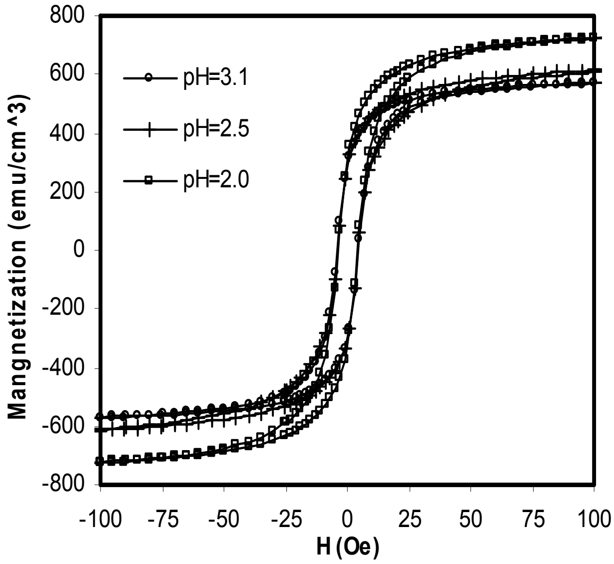

Fig. 3. Hysteresis loops of Ni-Fe films electrodeposited at different pH levels

The effect of electrolyte pH on the magnetic properties of the films was studied by measuring the parallel and perpendicular histeresis loops using VSM. The in-plane hysteresis loops of Ni-Fe films prepared with different pH levels are shown in Fig. 3 and their coercivities, H_c, and saturation magnetisations, M_s, are also presented in Table 1. H_c values of the films are around 4.0 Oe. M_s of the films deposited at low pH is larger than that of the films at high pH. M_s values of the films are in between the saturation magnetisation of the Ni (480 emu/cm^3) and Fe (1710 emu/cm^3) [16]. Magnetic analysis indicated that the saturation magnetisation of the films is affected by the electrolyte pH. Furthermore, the magnetic measurements revealed that in-plane hysteresis loops have a higher remanent magnetisation and lower saturation field than the perpendicular curves. This shows that the easy axis direction of the magnetisation is parallel to the film plane.

Table 1. Structural and magnetic data obtained from the Ni-Fe films grown at different pH levels

Samples pH (±0.1)	XRD relative integral peak intensities $I_{111}/I_{200}/I_{220}/I_{311}$	EDX analysis (% atom)		ICP analysis (% atom)		AMR (%)		Magnetic analysis	
		Ni	Fe	Ni	Fe	LMR	TMR	Hc (Oe)	Ms (emu/cm³⁾
3.1	83/18/100/3	78.22	21.78	79.51	20.49	5.2	5.2	4.32	617
2.5	100/17/18/5	74.84	25.16	75.56	24.44	3.7	3.7	4.12	720
2.0	100/15/25/6	73.02	26.98	70.00	30.00	2.4	2.4	3.91	777

5. Conclusions

Ni-Fe films were electrodeposited on polycrystalline Ti substrates from electrolytes with different pH levels. The films were found to have the fcc structure but the texture degree changes depending on the electrolyte pH. From XRD data when the electrolyte pH reduces the preferred crystal orientation changes from (220) to (111). All films exhibited AMR, and the AMR magnitude varies with the electrolyte pH. The saturation magnetization increased as the Fe content increased. The differences observed in the magnetotransport and magnetic properties were attributed to the microstructural changes and Ni:Fe ratio in the films caused by the electrolyte pH.

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