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EFFECT OF ELECTROLYTE TEMPERATURE ON MAGNETIC PROPERTIES OF Ni-Co-Cu ALLOY NANOFILMS GROWN ON SI SUBSTRATE BY ELECTRODEPOSITION METHOD

M.E. GHAZI[*], M. IZADIFARD, M. BAGHERZADEH

Physics Department, Shahrood University of Technology,
P.O. Box: 3619995161-316, Shahrood, Iran

In this work, Ni-Co-Cu nanofilms are grown on phosphor-doped Si substrate by electrodepostion technique at different electrolyte temperatures. The samples prepared are characterized by X-ray diffractometer (XRD), alternating gradient force magnetometer (AGFM), and flame atomic absoption spectroscopy (FAAS). The XRD patterns reveal that all films have FCC structure with (111) preferred orientation. No extra reflection due to secondary phases or individual elements of the alloy is observed. It is also shown that the crystal size increases with raising the electrolyte temperature. FAAS results show that increase in the electrolyte temperature causes decrease in Cu concentration and increase in Ni concentration. AGFM measurement results show that with increase in the electrolyte temperature, saturation magnetization increases and coercive field decreases.

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1. Introduction

Nowadays magnetic alloys have been attracted much attention due to their electrical, mechanical, magnetic, and magneto-optical properties [1]. Anisotropic magnetoresistance effect (AMR) and giant magnetoresistance effect are two the most interested properties which are used in magnetic field sensors and data storage media [2]. Magneto resistance has been attributed to the scattering of up- and down-spin carriers by magnetic clusters [3]. A variety of methods such as molecular beam epitaxy (MBE), thermal evaporation, sputtering, and electrodeposition have been used to grow magnetic thin films [4]. Amongst them, electrodeposition method is an interesting route due to the simplicity and cheapness of its setup performance of growth in atmospheric pressure and possibility to grow large and arbitrary shape multilayers.

On the other hand, the silicon single crystals is a good material as a substerate for growth of thin films. Due to the higher lattice constant of silicon (5.43 Å), as compared to lattice constants for metals such as Ni, Co, and Cu, adhesive forces between deposited layers and Si substrate are generaly weak [5]. Due to high resitance of Si substrate, growth rate on it in the electrodeposition method is slow [6]. Therefore, deposited metal on Si substrate grows as a 3D-islands [7]. Properties of thin films grown by electrodeposition method depend on several parameters such as ion concerntration, deposition mode, pH of electrolyte and its temperature, and substrate kind and its structure. In this work, Ni-Co-Cu thin films were grown on Si substrate by electrodepostion technique, and then their structural and magnetic properties were investigated.

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[*] Corresponding author: mghazi@shahroodut.ac.ir

2. Experimental

Phosphor-doped Si substrates with the (100) orientation and surface resistance of 25-30 Ω/□ were used as the working electrode. The back of these substrates were coated with Al of 0.2 µm thickness in order to get ohmic contact. To clean the substrates, they were put in boiling ethanol (96%) and then washed out for about 2 minutes in a solution containing HF, HNO_3, CH_3COOH, and deionized (DI) water, respectively. Finally, they were dried using nitrogen gas.

The electrolyte solution contained 0.025 $mol.dm^{-3}$ of $NiSO_4.6H_2O$, 0.025 $mol.dm^{-3}$ of $CoSO_4.7H_2O$, and 0.003 $mol.dm^{-3}$ of $CuSO_4.5H_2O$. Boric acid (30 $gr.dm^{-3}$) as a buffer,0.50 $mol.dm^{-3}$ Na3Cit reductant [10], and 0.0075 $mol.dm^{-3}$ Saccharin for increasing adhesive forces between film and substrate and improvement of the film quality were added to the electrolyte solution [11]. All compositions were solved in DI water. The deposition process was performed in a three-electrode bath using a computer-controlized potentiostat model BHP-2063. A 3 cm × 3 cm Pt sheet was used as a secondary electrode, and a saturated Calomel electrode as a reference electrode. Ni-Co-Cu films were prepared from electrolytes at three different temperatures. The diffusion coefficient and deposited material flow normally increase as the electrolyte temperature increases. The thin film structure and its crystallographic phase were investigated using XRD model Brucker AXS with Cu K_α line (1.5406 Å). To determine precentage of elements in the samples studied, FAAS was used. Magnetic properties of the films were studied using an AGFM.

3. Results and discussion

The Ni-Co-Cu alloy films were grown at the three electrolyte temperatures 45, 55, and 65 °C, respectively. Deposition voltage was set at -1.1 V. Thickness of the films was around 100 nm, which was calculated from Faraday law. With increase in electrolyte temperatures from 45 °C, pH values reduced from 4.8 to 3.6, due to evaporation of solution. XRD patterns of the films grown at different temperatures are shown in Figures 1-a, 1-b, and 1-c.

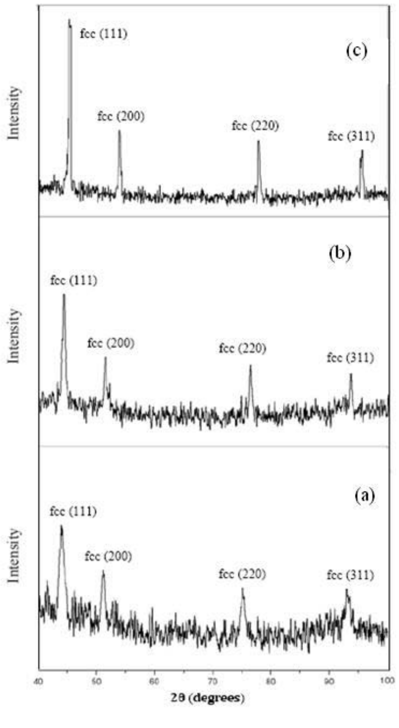

Fig. 1. XRD patterns for the films deposited at different electrolyte temperatures: a) 45 ℃, b) 55 ℃, and c) 65 ℃.

All the films had the FCC structure with the (111) preferred orientation, and there were no peaks associated with secondary phase or other individual metals in the alloy. As it can be seen in the figures, relative intensity of peaks, relative to preferred orientation, increases with raising the electrolyte temperature. Position of the peaks also moves towards higher angles by increasing electrolyte temperature; this indicates decrease in Cu percentage in the alloy. XRD patterns were used to find peak positions, lattice constant, crystal size, and strain. The results were summarized in Table 1. Calculated grain size shows that it increases by raising electrolyte temperature, indicating improvement in the film crystal structure. The film prepared at one of the two temperatures higher than 45 °C displays higher strain.

Table 1. Peak position (2θ), lattice constant (a), grain size (D), and strain (ε) of Ni-Co-Cu alloy films grown at different electrolyte temperatures.

ε	D (nm)	a (Å)	2θ (311) (deg.)	2θ (220) (deg.)	2θ (200) (deg.)	2θ (111) (deg.)	Electrolyte temperature (°C)
0.346	47.25	3.547	93.103	75.174	51.161	44.75	45
0.347	74.63	3.542	93.468	75.837	51.682	44.389	55
0.349	103.11	3.533	95.620	77.936	54.234	46.175	65

To determine precentage of the elements present in deposited films, FAAS was employed. The results were tabulated in Table 2. These results show that increase in electrolyte temperature causes decrease in Cu concentration and increase in Ni concentration.

Table 2. Precentage of elements in Ni-Co-Cu alloy films prepared at different electrolyte temperatures.

wt% Ni	wt% Co	wt% Cu	Electrolyte temperature (°C)
17	35	48	45
21	34	45	55
25	33	42	65

To investigate the magnetic properties of the films, AGFM measurements were conducted at room temperature. Magnetic field was applied along the film surfaces. Figures 2 (a, b, and c) show that hysteresis loops of the films deposited at the different electrolyte temperatures of 45 °C, 55 °C, and 65 °C, respectively. The saturation magnetization, coercive field, and remnant magnetization extracted from these figures are summarized in Table 3.

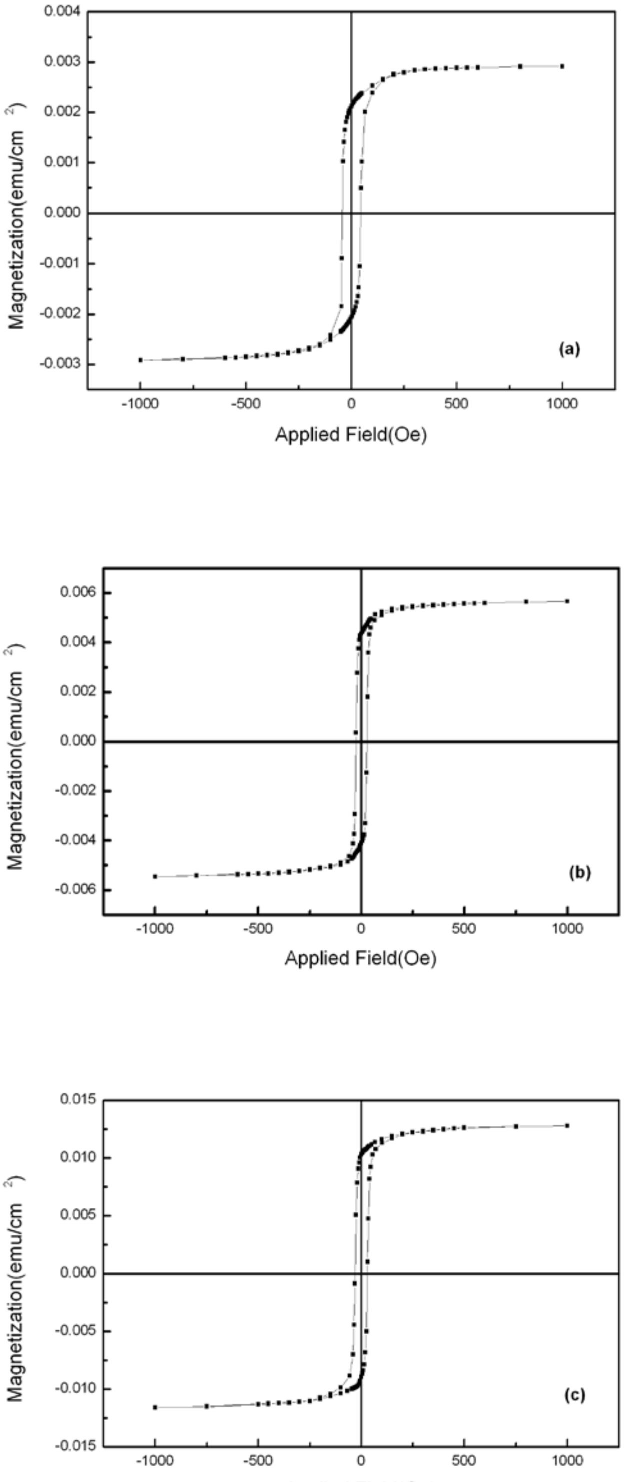

Fig. 2. Hystersis loops of the Ni-Co-Cu films deposited at different electrolyte temperatures: a) 45 ℃, b) 55 ℃, and c) 65 ℃, measured at room temperature.

As the values for saturation magnetization show, electrolyte temperature has an important role in the saturation magnetization of the film. Saturation magnetization of the sample prepared at the electrolyte temperature of 65 °C rises up to around four times. This may be due to increase in Ni concentration in alloy with increasing electrolyte temperature (see Table 2) and increase in grain size [12]. The coercive field decreases with increase in the electrolyte temperature, which may be due to decrease in Cu concentration. Increase in saturation magnetization with change in concentration of elements was also reported for Co-Ni-Fe alloy, and was attributed to redistribution of the electronic orbitals [13].

Table 3. Results of hysteresis measurements for the Ni-Co-Cu/Si films deposited at different electrolyte temperatures.

Coercive field (H_c /Oe)	Ratio of $S=M_r / M_s$	Remnant magnetization M_r (emu.cm^{-2})	Saturation magnetization M_s (emu.cm^{-2})	Electrolyte temperature (°C)
42.5	0.726	0.0021	0.0029	45
27	0.7707	0.0043	0.0055	55
29	0.8053	0.0095	0.0126	65

Saturation magnetization of a compound can be expressed as a linear combination of saturation magnetizations of individual elements [13]:

$$M_s^{cal.} = M_s^{Ni} C^{Ni} + M_s^{Co} C^{Co} \qquad (1)$$

where M_s^X is saturation magnetization of pure Co or Ni, and C^X is percentage of elements present in the compound. Saturation magnetizations of FCC Co and Ni are 1440 and 485 emu.cm^{-3}, respectively. Using these values and the equation, saturation magnetization of the alloy was calculated (Table 4). Comparison between the observed and calculated values shows that only for electrolyte at 55 °C these two are nearly the same but there are big differences between the two values at the other two temperatures. These may arise from a structural rearrangement with variation of the chemical composition.

Table 4. Observed and calculated values for saturation magnetization.

$M_s^{Cal.}$ (emu.cm^{-3})	$M_s^{obs.}$ (emu.cm^{-3})	Electrolyte temperature (°C)
586.45	292	45
591.45	567	55
596.45	1279	65

4. Conclusion

In this work, Ni-Co-Cu nanofilms were grown on phosphor-doped Si substrate by electrodepostion technique at different electrolyte temperatures. Prepared samples were characterized by different techniques. The film structures and their crystallographic phase were investigated by XRD measurements. Concentrations of the film elements were obtained by FAAS. Magnetic properties of the films were studied by an AGFM. The XRD patterns reveal that all films have FCC structure with the (111) preferred orientation. No extra reflection due to secondary phases or individual elements of the alloy was observed. XRD measurements also show that crystal size increases with raising electrolyte temperature. The film prepared at one of the two temperatures higher than 45 ^{o}C also displays higher strain. The FAAS results show that increase in electrolyte temperature causes decrease in Cu concentration and increase in Ni concentration. The results for AGFM measurements show that with increase in electrolyte temperature, saturation magnetization increases and coercive field decreases.

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