Growth of Electrodeposited Ni-Co and Fe-Co Magnetic Films on Cu Substrates

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Abstract. This paper reports on synthesis of Ni-Co alloy films using electrodeposition technique. The morphology and crystalline characteristics of the films have demonstrated dependence on deposition parameters. The electrolyte temperature and pH have shown to have the most influence on the crystallographic structure of the film. The microstructure, crystallographic texture and magnetic properties are studied by varying the substrate pretreatment and deposition parameters. The dependence of the surface morphology has been investigated by employing SEM, XRD, EDAX and AFM. X-ray diffraction analyses have revealed the polycrystalline nature of the films, the average crystallite size, and the crystal orientation that has dependence on temperature and pH of the electrolyte. VSM analysis has revealed that the coercivity has also dependence on temperature and pH of the bath due to variation of crystal orientation and crystallite size of the films on copper substrates.

1. Introduction

Growth of thin ferromagnetic films and required magnetism of fcc Ni and fcc or hcp Co in the form of metals or alloys on Cu (100) and Cu (111) surfaces have been a matter for detailed investigations [1, 2]. For technical reasons most current applications of magnetic thin films, e.g. sensors for disk drives and magnetic random access memory, involve the deposition of fcc films with (111) texture. Ni–Co alloy coatings have been widely used as recording head materials in computer hard drive industries or as a kind of typical magnetic layers for micro electrical mechanical system, MEMS. The investigations on the electrodeposited Ni–Co alloys have shown that their microstructure and properties were found to depend strongly on the Co content. It is extremely difficult to obtain good grown layers in these films because they are susceptible to the incorporation of stacking faults which form at the cost of very little energy. Such structural defects appear to have a strong influence on the magnetic coupling. The processing techniques introduced so far for producing nanocrystalline materials have intended to

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minimize this problem. Among these, electrodeposition has been recognized as a technologically feasible and economically superior technique for production of nanocrystalline materials [3, 4, 5]. The investigations on the electrodeposited Ni–Co alloys have shown that their microstructure and properties were found to depend strongly on the Co content, which can be controlled by the experimental parameters, such as bath composition, temperature, pH value, and current density, etc [6].

2. Experimental

2.1. Substrate preparation and Electrodeposition.
The Ni-Co films were electrodeposited on pretreated copper substrates that were initially abraded to the desired thickness using SiC paper of 1200 and 2400 mesh using Phoenix 4000 preparation system with base plate speed of 150-200 r.p.m for 5 – 7 minutes under 1.5 to 2 mbar of force. To remove residual copper particles from the surface, the substrates were cleaned in a boiling water system for five minutes then rinsed with DI water and finally dried using nitrogen gun. Afterwards the substrates were polished with diamond suspension of particles (1 – 3 µm). At the end of each stage the samples were made particle free. To improve the surface condition the substrates were electropolished using stainless steel electrode as cathode at 1.6 volts for 12 minutes in a solution of Phosphoric acid (density = 1.75 g Cm⁻³) and distilled water, in proportion of 700 ml and 300 ml respectively at room temperature. Figure 1 shows SEM images of Cu substrate after mechanical and electropolishing.

Deposition of Ni-Co films on copper substrate were performed using a conventional sulfate bath electrodeposition process according to Table 1. Solartron Potentiostat 1285 was employed to control the deposition parameters. Analogue sweep type in galvanostatic mode of operation with 3.8 A dm⁻¹ [8] was set up during the deposition. The pH of the electrolyte was controlled with H₂SO₄ for different samples and the temperature was set between 20 to 70 °C at appropriate intervals. After depositions the samples were thoroughly washed with deionized water and dried with nitrogen gun. The samples were examined by SEM, EDAX, XRD and AFM. XRD measurements were carried out using a Philips X’pert pro MPD (Multi Purpose Diffractometer) with Cu-Kα radiation with Ni filter in θ/2θ mode. The coercivity of the samples were measured using a Vibrating Sample Magnetometer (VSM) up to the applied field range of 301.2 kA m⁻¹ (3784 Oe) using Lab view 4+1 software to trace and analyze the magnetic hysteresis loop of the thin films deposited on Cu substrate.

| Sample | Component salts | Concentration (g l⁻¹) | pH | Temp(°C) | Time (Min) |
|--------|-----------------|-----------------------|----|----------|------------|
| Ni-Co  | NiSO₄·6H₂O      | 60                    | 2-4| 40-70    | 30-120     |
|        | NiCl₂·6H₂O      | 50                    |    |          |            |
|        | CoSO₄·7H₂O      | 29                    |    |          |            |
|        | H₃BO₃           | 30                    |    |          |            |

Figure 1. SEM image of Cu substrate (a) before and (b) after electropolishing.
3. Results and discussion

3.1. SEM and EDAX analysis and Characterization of Ni-Co films
Deposited films are investigated using SEM and EDAX analysis that has revealed the surface texture and alloy content respectively. Through out the electroplating of Ni-Co alloy films the molar concentration of the contents are kept constant, however, the EDAX result revealed that Ni and Co concentration varied between 58% to 90% for 120 minutes and 60 minutes respectively. This is shown in figure 2. The presence of small amount Fe in the Ni-Co film detected in EDAX plot shown in Figure 2 is due to the contamination formed by the stainless steel electrode used for electrodeposition.

![Variation of Ni and Co concentration on deposited film on Cu for the same pH of 3.6 and temperature of 66 for (a) 60 min. and (b) 120 min.](image)

Ni-Co grain size increased from 64.1 nm with a lattice constant of 1.75 Å to 64.2 nm with a lattice constant of 2.03 Å as the pH of the bath increased from 2 to 3. Figure 3 is the SEM image of the grain size on the surface of the Ni-Co surface. It was also noticed that change in pH of the electrolyte had effect on the plane of the film growth as this change was from (200) to (111) in above case resulting a significant reduction in coercivity from 17.8 kA m⁻¹ to 8.1 kA m⁻¹.

![SEM results for Ni-Co films on Cu (a) and (b) electrodeposited at 66 °C for 60 minutes with pH 3 and 2 respectively (c) and (d) electrodeposited with pH 2.8 at 66 °C for 60 and 90 minutes respectively.](image)

In a recent work on electrodeposition of Ni-Co film on copper substrate high coercivity ranging between 159.2 kA m⁻¹ to 238.8 kA m⁻¹ was reported [2] where as, our samples showed low coercivity varying between 8.1 kAm⁻¹ to 19.5 KAm⁻¹. However, on a similar work a range of coercivity between 1.6 kA m⁻¹ to 2.4 kA m⁻¹ was reported [9]. Table 2 summarizes details of Ni-Co samples under investigation and the effect of electrolyte pH on structural and magnetic coercivity of the grown film. In all cases the grain or the crystallite size changed with pH. As expected, as the grain size changed consequently, the film thickness increased.

3.2. X-Ray Diffractometry and magnetic characterization
Fig. 4 shows the XRD analyses of Ni-Co samples grown under different pH values. The preferred crystal orientation of the sample observed to be (111) while depositing from bath of pH at 3.6 and 3 at
Table 2. A summary of the effect of pH and temperature of the electrolyte on structure and magnetic coercivity of Ni-Co films grown on Cu substrate

| Sample Number | composition of films on Substrate | pH | Temperature (°C) | Time (min) | film thickness (µm) | Coercivity (KA m⁻¹) | Grain size (nm) | Lattice strain (%) | Lattice constant (Å) |
|----------------|----------------------------------|----|-----------------|-----------|---------------------|----------------------|------------------|------------------|-------------------|
| 1              | Ni-Co                            | 3.6| 66              | 60        | 44.2                | 17.8                 | 39.6             | 0.231            | 2.03 (111)        |
| 14             | Ni-Co                            | 3  | 66              | 60        | 51.5                | 8.1                  | 64.2             | 0.210            | 2.03 (111)        |
| 6              | Ni-Co                            | 2.8| 66              | 60        | 56                  | 8.1                  | 43.6             | 0.087            | 2.03 (111)        |
| 15             | Ni-Co                            | 2  | 66              | 60        | 56                  | 17.8                 | 64.1             | 0.124            | 1.75 (200)        |

temperature of 66 °C for 60 minutes. This orientation changes to (220) at pH 2.8 and to (200) from bath of pH 2 at the same temperature and time. The relative intensity of (111) orientation reduces significantly as pH reduces by 0.2 from pH 3. Ni-Co films on Cu substrate show a varying peak width ranging from 0.00145° to 0.0547° for the plane with 100% intensity for the pH values between 2 and 3.6. Fig. 5 shows the effect of pH on the average crystallite size in nanometric scale that is found to be in the range of 64.1 nm to 84.3 nm. The average crystallite size is found to be the largest for deposition at pH of 3.6 while depositing from 66°C bath for 60 minutes. The size of the crystallite starts to increase between pH 2.8 to 3.6 after a decrease from pH 2. From the plot of lattice strain in Fig. 5, it is evident that stress in the film is highest at pH 3.6 and lowest at pH 2.8. The coercivity values plotted in the same figure shows that coercivity is highest for largest grain size sample. This is due the stress in the film. Apart from these discrepancies, grain size dependence of coercivity agrees with the model proposed by Herzer [11] for nanocrystalline soft magnetic materials. Figure 6 shows that average crystallite size varies in nanometric scale between 39.6 nm to 87.3 nm when temperature varies from 40 °C to 70 °C. The average crystallite size is found to be largest at 60 °C and smallest at 66 °C. The Ni-Co films on Cu substrate show a varying peak width ranging from 0.00129° to 0.00894° depending on the pH of the electrolyte at temperature 66 °C and 60 minutes deposition time. From the plot of lattice strain in Fig. 6, it is evident that stress in the film is lowest at 60 °C then increases to its highest value at 66°C. The coercivity values plotted in the same figure shows that coercivity only varies slightly with grain size due the stress in the film for lower grain size sample at 50 °C.

Figure 4. XRD pattern showing the effect of pH on Ni-Co film deposited on Cu with different preferred orientation at different pH values.

Figure 5. Effect of electrolyte pH on the average crystallite size, lattice strain and magnetic coercivity of Ni-Co films on Cu substrate (bath temperature: 66 °C and deposition time: 60 minutes).
The effect of substrate condition on magnetic properties of films was suited from two distinctive points of view. First, it was noted that substrates with higher degree of polishing allows more uniform film deposition with less degree of surface roughness. The XRD analysis of these films indicated larger grains on the surface than the ones grown on substrates with no electropolishing finish. It seems to be a disadvantage for substrate with high degree of polishing. On several experiments it was noted that the films started to peel off from the rim of the Cu substrates indicating surface adhesion problem. The adhesion problem seemed to be rectified by annealing the substrate in a moderate temperature for few hours. Second, some forces of 10, 20, and 30 bars were applied to the substrates prior to polishing and the effect on magnetic properties, in general was in agreement with previously report [12].

3. Conclusion
X-ray diffraction analysis revealed that the films with nanometer size grains of Ni-Co, Fe-Co, and Co can be grown on Cu substrate with the average sizes ranging from 24.2 nm to 84.3 nm that depends on the pH and temperature of the electrolytes. The smallest grain size found to be in Fe-Co alloy with 24.2 nm in dimension. This is observed in the temperature range of 25 °C and 40 °C and pH varying from 2 to 3.4. All the fabricated films show columnar growth and preferential crystallographic orientation of certain plane with pH and temperature variation. In Ni-Co films (111) plane dominates at pH 3.6 and (200) at pH 2. In Fe-Co films (111) plane dominates at deposition temperature of 30 °C and 40 °C whereas, (111) is most prominent at 40°C. This plane also shows strongest intensity in Fe-Co at pH between 2.2 and 2.8. It may be concluded that the process parameters such as temperature and pH has an influence on the preferred orientation of planes and the size of the nanocrystals or grains of electrodeposited. Magnetic coercivity $H_c$ values at pH of 2 are compared and in Co films found to be about 7.5 times higher than in Fe-Co films and in Ni-Co films $H_c$ found to be about 6.5 times higher than Fe-Co suggesting that Fe-Co alloys to have lowest magnetic coercivity among the Ni, Fe, Co alloys. Generally, the stress in the film all three types of film seems to control the magnitude of $H_c$ values and in some cases this value shows more than ten times higher value than its bulk counter part.

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