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# Electrodeposited cobalt films: The effect of deposition potentials on the film properties

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A series of cobalt films were deposited on copper substrates at different deposition potentials between -1.0 V and -1.6 V and their properties were investigated. The proper deposition potentials were obtained from the cyclic voltammetry method. The magnetic analysis of the films showed the saturation magnetization increased and the coercivity decreased as the deposition potential increased. It was also observed that the easy axis direction of magnetization was parallel to the film plane for all films. X-ray diffraction results revealed that all films had a mixture of hexagonal close-packed (hcp) and face-centred cubic (fcc) phases, and the hcp/fcc ratio increased as the deposition potential increased. Scanning electron microscope images showed that the morphology changed from ridged grains to a smooth surface with the increase of deposition potential. The results showed that the changes in magnetic and structural properties of cobalt films were substantially depend on the variation of deposition potentials. Therefore, the change of the potentials was seen to control the properties of the films and hence their properties could be modified for desired purpose.

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*Keywords:* Co films, Electrodeposition, Magnetic properties, Crystal structure and morphology

## 1. Introduction

In recent years, it is well known that ferromagnetic films on metallic substrates have played an important role in technological applications such as microactuators, micromotors and sensors [1, 2]. Magnetic films have been produced by conventional techniques like molecular beam epitaxy, sputtering, evaporation, electrodeposition etc. [3-7]. Among these techniques, electrodeposition is preferable because it does not require a vacuum system, and is a simple production process with easy control of deposition parameters [8]. Using electrodeposition, magnetic films with desired properties, shape and thickness can be obtained for technological applications such as sensors, microactuators and micromotors. In order to produce the films with such properties, the films should be obtained at certain deposition conditions. In electrodeposition technique, magnetic, structural and morphological properties of deposits depend on the electrodeposition parameters [9], especially deposition potentials [10, 11].

The cobalt properties as corrosion resistance [3], high coercivity and high saturation magnetization [12] make cobalt useful and feasible material for potential applications in magnetic media devices. More importantly, magnetic material as cobalt plays an important role in magnetic sensors, microactuators, micromotors and data storage devices [13-15]. Up to now, the investigations of plating Co films deposited on various substrates such as Cu [16-19], Au [20-22], Si [18, 23, 24], and KIT-6/ITO [25] have been focused on substrate dependence of properties of the films. The work on the cobalt films deposited on copper substrate mainly concentrated on the structural properties as follows: The effect of diluted

sulphuric acid on the formation of Co films on polycrystalline copper was investigated [16]. And, the influence of scratched substrate surface on patterned Co layers was studied with the use of the Scanning Electron Microscopy and X-Ray Diffraction [17]. The thin Co films of 100-nm thickness on Si and on Cu substrates were analysed depending on the film thickness at high and low pH [18]. Finally, the nucleation, surface growth and roughening of cobalt electrodeposits on a polycrystalline copper and on amorphous graphite substrates were studied using electrochemical techniques and surface imaging by Atomic Force Microscopy [19]. On the other hand, only a few studies have dealt with the relation of the deposition parameters except for deposition potential to the magnetic properties of pure electrodeposited Co films [16, 26, 27]. Therefore, under study, the relation between deposition potentials and magnetic, structural and morphological properties of the pure cobalt films electrodeposited on polycrystalline copper substrate was studied. It was seen that the film properties can be controlled and modified by changing deposition potentials.

## 2. Experimental

Cobalt films were electrodeposited on (110) textured polycrystalline copper substrates under potentiostatic conditions. The electrolyte used to deposit the films contains 0.5 M cobalt sulphate and 0.3 M boric acid. Electrodeposition was carried out in a conventional three electrode cell using a Potentiostat/Galvanostat (EGG model 362). The working electrode was copper substrate. Prior to electrodeposition, copper substrate was covered with an electroplating tape, except for an area of 1.21 cm<sup>2</sup> and then it was electrochemically polished in 50 vol. %

orthophosphoric acid. Subsequently, it was washed in 10 vol. % sulphuric acid and distilled water, respectively. Counter electrode was a Platinum electrode. A saturated calomel electrode (SCE) was used as reference electrode and all potentials were referred to this electrode.

The cyclic voltammetry (CV) method was used to determine the cathodic potentials to deposit the films. Voltammetric experiments were performed in a three electrode cell from initial potential of +1.0 V to -1.8 V using a scan rate of 20 mV/s. According to the CV results, the films were deposited at different potentials ranging from -1.0 V to -1.6 V at room temperature. The pH was  $2.5 \pm 0.1$  and the nominal film thickness was 5  $\mu\text{m}$ . Thicknesses of the films were calculated by Faraday's Law [7] and controlled by the computer. In order to investigate the nucleation and growth mechanism of the films current-time transients were recorded during deposition.

A vibrating sample magnetometer (ADE EV9 model VSM) was used for magnetic measurements. A magnetic field up to 20 kOe was applied both parallel and perpendicular to the film plane at room temperature. Structural analysis was performed by X-ray diffraction (XRD) with a Rigaku rint-2200 diffractometer using  $\text{CuK}\alpha$  radiation. The scan was performed between  $40^\circ$  and  $100^\circ$ . Film compositions were determined by energy dispersive X-ray spectroscopy (EDX) and morphology of the films

was examined with a Zeiss Supra 50 Vp model scanning electron microscope (SEM). The electrolyte was elementally analyzed by Perkin Elmer Optima 3100XL model inductively coupled plasma atomic emission spectrometry (ICP-AES).

### 3. Results and discussion

In order to choose the appropriate deposition potentials, the electrolyte was characterized by the CV. Figure 1 shows the stabilized cyclic voltammogram obtained for the electrolyte used to deposit cobalt films. The curve shows the cathodic and anodic peaks associated to the deposition and dissolution of cobalt, respectively. There is no considerable current flowing in the potential region between +1.0 V and -0.9 V. Cobalt deposition begins at around -0.9 V. As the absolute value of cathode potential increases from -0.9 V to -1.2 V, the current also increases. Between -1.2 V and -1.5 V, the increase of current slows down. After -1.5 V, it begins to increase with the increase of the potential. When the scan is reversed, the nucleation loop is observed. At around +0.2 V an oxidation peak of cobalt is detected. According to these results and the appearance of the films, deposition potential range was decided to be between -1.0 V and -1.6 V. The selected potential values are listed in Table 1.

Table 1 Elemental and structural analysis and magnetic results of electrodeposited Co films.

| Deposition potential (V) | Crystal structure analysis (XRD) |       |         | Magnetic measurements (VSM)  |            |           |
|--------------------------|----------------------------------|-------|---------|------------------------------|------------|-----------|
|                          | % hcp                            | % fcc | hcp/fcc | $M_s$ (emu/cm <sup>3</sup> ) | $H_c$ (Oe) | $M_r/M_s$ |
| -1.0                     | 33                               | 67    | 0.49    | 884                          | 48         | 0.46      |
| -1.3                     | 39                               | 61    | 0.64    | 907                          | 39         | 0.48      |
| -1.6                     | 52                               | 48    | 1.08    | 965                          | 21         | 0.66      |

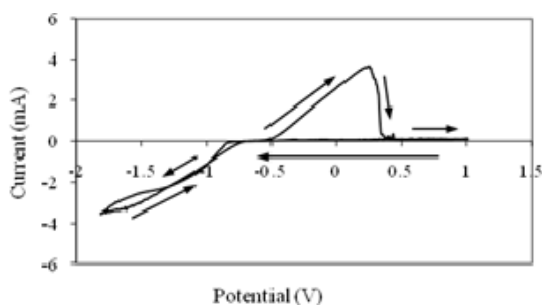


Fig. 1 Cyclic voltammogram of the electrolyte used to deposit cobalt films (Arrows show the scan direction.).

The current-time transients were also recorded to understand the nucleation and growth mechanism of cobalt films. Figure 2 shows the current-time transients of the films for the first 100 secs. All transients show an initial increase of current due to the nucleation process. The constant current flow afterwards indicates the proper diffusion limited growth during deposition. The current value increases as the deposition potential increases and the stable current value of each transient is consistent with its deposition potential.

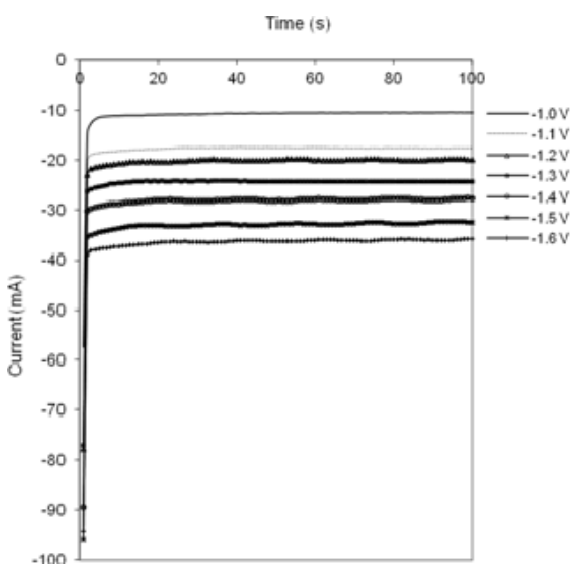


Fig. 2 Current-time transients of cobalt films deposited at different deposition potentials.

In-plane and perpendicular hysteresis loops of the films produced at different deposition potentials are shown in Figure 3. Magnetic results of the in-plane loops are presented in Table 1. In the table, coercivity,  $H_c$  decreases from 48 Oe to 21 Oe whereas saturation magnetization,  $M_s$  increases from 884  $\text{emu}/\text{cm}^3$  to 965  $\text{emu}/\text{cm}^3$  as the deposition potential increases. In a study [18],  $H_c$  of the Co on Cu films decreases approximately linearly with the film thickness, ranging from 192 Oe at 2.5 nm to 25 Oe at 100 nm.  $M_s$  of the films are lower than the value of bulk cobalt (1422  $\text{emu}/\text{cm}^3$  at 20 °C) [12]. Squareness,  $M_r/M_s$  also increases with the increase of deposition potential. For the investigation of the in-plane anisotropy in the films, as seen in Figure 3, in-plane hysteresis loop of the film (-1.0 V) has higher remanent magnetization and lower saturation field than the perpendicular one indicating the easy axis direction is in the film plane. As a result of demagnetising effect, the shape anisotropy forces the films to have a planar easy axis. No perpendicular anisotropy has been detected for the rest of Co films.

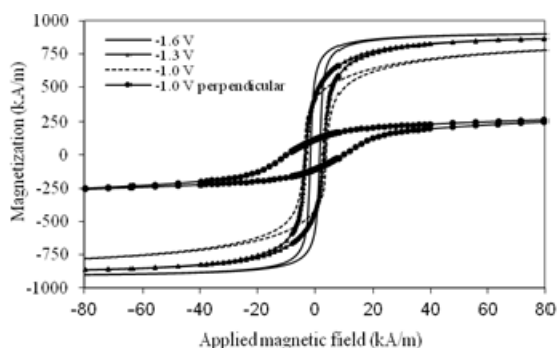


Fig. 3 Parallel hysteresis loops of cobalt films deposited at -1.0 V, -1.3 V, -1.6 V and perpendicular loop of the film deposited at -1.0 V.

XRD patterns of cobalt films deposited at -1.0 V, -1.3 V and -1.6 V are shown in Figure 4. The substrate peaks of (200), (220) and (311) planes which were seen at  $2\theta \approx 51^\circ$ ,  $73^\circ$  and  $89^\circ$ , respectively are marked as S(hkl) in the patterns, the peaks of face centered cubic (fcc) (111), (200) and (220) planes were seen at  $2\theta \approx 43^\circ$ ,  $52^\circ$  and  $74^\circ$ , respectively. An additional (311) peak was also appeared in the films deposited at -1.0 V and -1.6 V. Beside, hexagonal close packed (hcp) (10.0), (00.2) and (10.1) peaks were observed at all patterns. However, in a study [28] hcp at high pH ( $\sim 5.7$ ) and fcc at low pH ( $\sim 1.6$ ) structures were observed in electrodeposited cobalt. Under study, both phases are present;  $\alpha$ -Co (hcp) and  $\beta$ -Co (fcc) in each pattern of films but the degree of hcp to fcc phase ratio exhibited a dependence on the deposition potential. The hcp/fcc ratio are calculated using the total integral intensities of hcp peaks to those of fcc ones and shown in Table 1.  $M_s$  increases and  $H_c$  decreases which might be attributed to the increase of hcp/fcc ratio from 0.49 to 1.08 caused by the deposition potential.

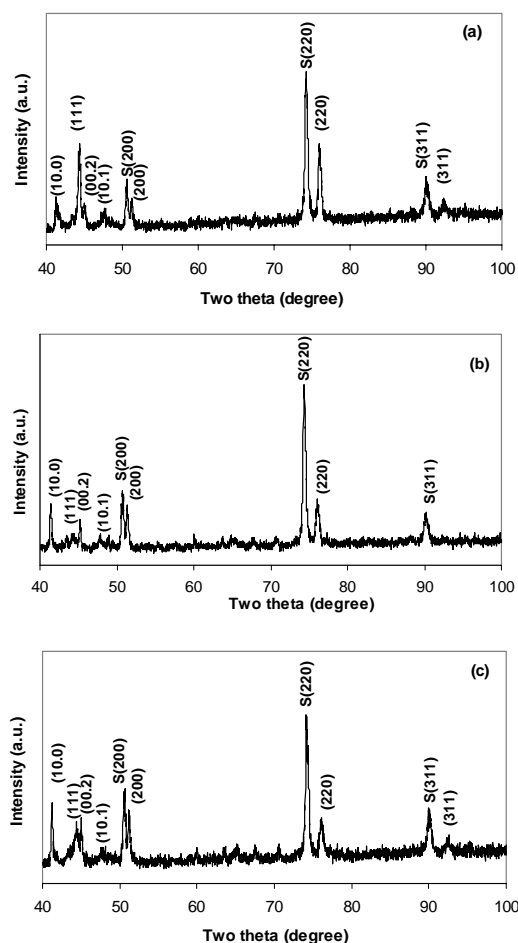


Fig. 4 XRD patterns of Co films deposited at a) -1.0 V, b) -1.3 V, c) -1.6 V. S(hkl): Substrate peaks. Co(fcc): (111), (200), (220) and (311) peaks. Co(hcp): (10.0), (00.2) and (10.2) peaks.

The impurities in the electrolyte can be found as an additional element in the films [29]. In order to clear whether there are any impurities in the prepared electrolyte or not, the ICP-AES analysis was performed. Elemental analysis of the electrolyte disclosed that impurities in the electrolyte were found to be under the detection limits. Besides, to the compositional analysis of the film by the EDX, at a selected deposition potential (-1.6 V), it was seen that pure cobalt was only detected in the films.

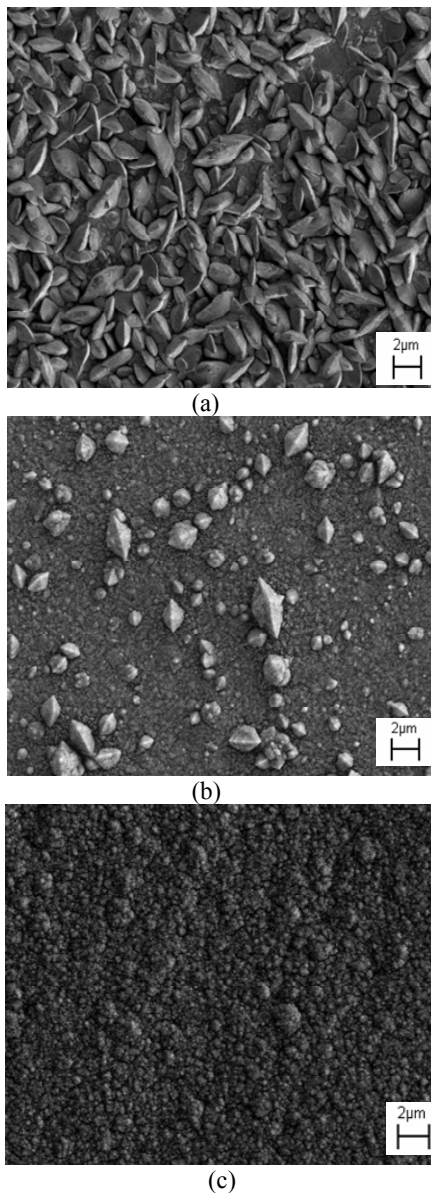


Fig. 5. SEM images of a) Cu substrate prior to deposition and Co films grown at b) -1.0 V, c) -1.3 V, d) -1.6 V.

SEM micrographs of the films are given in Fig. 5. As can be seen from Figure 5a, at low deposition potential (-1.0 V), the morphology is characterized by randomly arranged 1-3  $\mu\text{m}$  ridged grains. Next, at -1.3 V (Figure 5b), the grains become less with some smaller ones. Finally, at

high deposition potential (-1.6 V), the grains disappeared and a smooth surface was observed, see Figure 5c. Surface morphology of the films such as the number of the grains was found to depend on the deposition potential.

#### 4. Conclusions

Cobalt films were electrodeposited at different deposition potentials between -1.0 V and -1.6 V. Saturation magnetization of the films increased and the coercivity of them decreased with the increase of deposition potential. All films showed planar anisotropy. Magnetic properties exhibited a dependence on deposition potentials. All films displayed a mixture of hcp and fcc phases with a degree of hcp/fcc ratio depending on the deposition potentials. However, percentage of hcp phase decreased with decreasing deposition potentials and grainy structure was appeared at low deposition potentials of -1.3V and -1.0V. With the increase of deposition potential, hcp/fcc ratio decreased and consequently the morphology turned to smooth surface. It was observed that the magnetic, structural and morphological properties of the films are considerably affected by the deposition potential.

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