

Electrodeposited Cobalt Films: Alteration Caused by the Electrolyte pH

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Abstract Cobalt (Co) films were electrodeposited on polycrystalline copper substrates at different pH values. It is observed that the crystal structure of the films converts from hexagonal close-packed (hcp) to a mixed phase of face centered cubic and hcp as the electrolyte pH decreases. The grain size calculated from the X-ray diffraction patterns decreases with the decrease of electrolyte pH. The surface of the films grown at a high pH is more uniform than that of the films grown at a low pH. The saturation magnetization and the coercivity decrease as the electrolyte pH decreases. The high coercivity value at high pH corresponds to the hcp crystal structure of the films as well as the large grain size of Co clusters. Magnetic measurements also reveal that the easy axis direction of magnetization is parallel to the film plane for all films since the higher remanent magnetization and lower saturation field are observed in parallel hysteresis loops.

Keywords Cobalt films · Crystal structure · Electrodeposition · Magnetic properties

1 Introduction

Since magnetic films present important applications in data storage devices, sensor and actuator technology, and write-read heads, they have been produced by using different

techniques such as; molecular beam epitaxy, thermal evaporation, sputtering, and electrodeposition [1–3]. Electrodeposition is a simple electrochemical process which does not require vacuum system and provide the production of high quality films in a cheaper and easier way at room temperature and pressure [4]. The properties of the electrodeposited films are significantly affected by deposition parameters. One of the most effective parameters is the electrolyte pH [5]. Thus, the purpose of this study is to investigate the structural and magnetic properties of cobalt films grown on copper substrates at different pH levels. It was observed that the properties of the films were considerably affected by the electrolyte pH.

2 Experimental

The electrodeposition system consists of a potentiostat/galvanostat (EGG model 362) and an electrochemical cell with three electrodes. (110) textured copper (Cu) substrates were used as cathodes and a platinum (Pt) plate as the anode. The reference electrode was a saturated calomel electrode (SCE). All experiments were carried out at room temperature. Prior to deposition, substrate surface was covered with electroplating tape, except for the area to be deposited. The area was electropolished in 50% H₃PO₄. An electrolyte consisting of 0.5 M CoSO₄·7H₂O and 0.3 M H₃BO₃ was prepared. The films were produced at high pH (3.1) and low pH (2.5) with the −1.5 V cathode potential. The charge amount required for the film thickness was calculated according to the Faraday law by assuming 100% current efficiency [6] and the nominal thickness of all films was fixed at 3 μm. True value of current efficiency may be less than 100% due to the hydrogen evolution at the cathode. However, the hydrogen evaluation during the Co deposition is not much observed

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and, therefore, it is assumed that the nominal thickness of the deposits is almost the real thickness of the films at both pH values. During the deposition process, the current was recorded as a function of time in order to control the stability of growth. After deposition, all films were stored in desiccators until characterization.

The structural analysis of the films was achieved using the X-ray diffraction technique (XRD, Rigaku Rint 2200) with $\text{CuK}\alpha$ radiation with scan step of 0.02° . The analysis of surface morphology was made by the scanning electron microscope (SEM, Zeiss Supra 50 Vp). Energy dispersive X-ray spectroscopy (EDX) was used to confirm the production of pure cobalt films. The magnetic measurements were performed with a commercial vibrating sample magnetometer (VSM, ADE Technologies EV9) at ± 20 kOe.

3 Results and discussion

To understand the growth characteristics of the films, the current-time transients were recorded during the deposition and given in Fig. 1. The current occurred during the deposition of the film that was grown at high pH (3.1) is slightly lower with respect to that of the film grown at low pH (2.5). This can be attributed to the increase of hydrogen ions in the electrolyte when pH is lower. It was seen that the films have the same type of growth modes at high and low pH values.

XRD measurements of Co films were done on their substrates and the results were summarized in Table 1. Figure 2

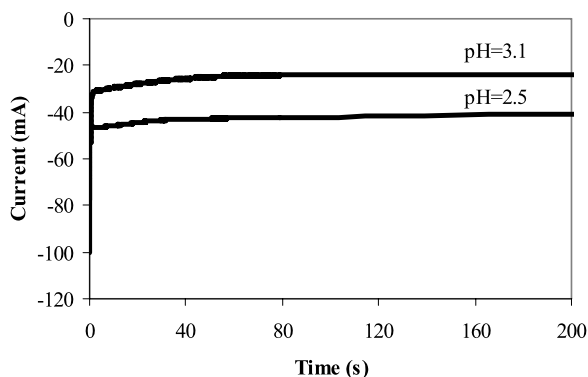


Fig. 1 Current-time transients of Co films deposited at high pH (3.1) and low pH (2.5) values

Table 1 Structural and magnetic properties of Co films

Electrolyte pH (± 0.1)	Crystal structure (XRD)		Magnetic measurements (VSM)		
	Crystal phase	Average grain size (nm)	$H_{c\parallel}$ (Oe)	$H_{c\perp}$ (Oe)	M_s (emu/cm^3)
3.1	hcp	70	49	215	1201
2.5	hcp + fcc	48	35	179	840

shows the XRD patterns of the films at high and low pH. The Cu substrate peaks were labeled as S(hkl) in the patterns and the (111), (200), (220) and (311) peaks of face centered cubic (fcc) structure of Cu were observed at $2\theta \approx 43^\circ$, 50° , 74° and 89° , respectively. It is seen from Fig. 2(a) that the film deposited at high pH has hexagonal close-packed (hcp) structure. The pattern includes the reflections from the planes (00.2) and (11.0) at around 44° and 75° , respectively. The preferential orientation is found to be (00.2). In Fig. 2(b), (00.2) peak of hcp structure weakened and (111) peak of fcc Co appeared at around 44° . The intensity of (11.0) peak at 75° is also weakened. The film deposited at low pH showed mixed phase of hcp + fcc and the preferential orientation for hcp is (00.2). The change observed in the crystal structure of the films may be ascribed to the presence of intermediate species such as hydrogen [7]. It is also known that at low pH values fcc phase can be seen in electrodeposited Co films [8, 9]. Lattice parameters were calculated using the least squares technique and found to be $a = (0.2507 \pm 0.0001)$ nm, $c = (0.4055 \pm 0.0002)$ nm for the film deposited at high pH and $a = (0.2512 \pm 0.0001)$ nm, $c = (0.4058 \pm 0.0002)$ nm for that at low pH. The mean grain sizes of the films were calculated according to the Scherrer equation [10] and given in Table 1. The average grain sizes for the films grown at high and low pH are 70 nm and 48 nm, respectively.

Figure 3(a) and 3(b) show the SEM images of films deposited at high and low pH levels, respectively. At high pH,

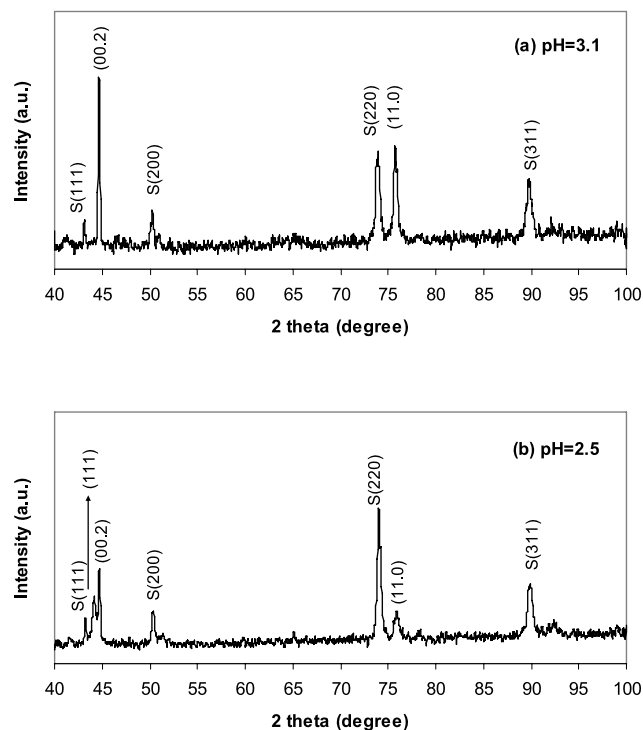


Fig. 2 XRD patterns of the Co films deposited at (a) high pH (3.1), (b) low pH (2.5). S(hkl) indicates the Cu substrate peaks

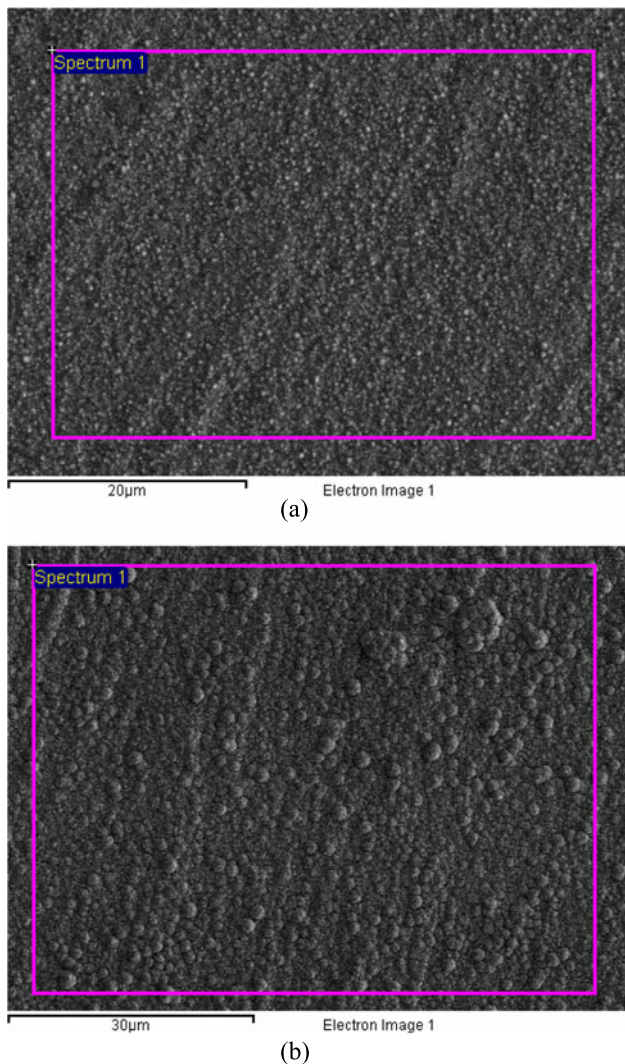


Fig. 3 SEM images of Co films deposited at (a) pH = 3.1 and (b) pH = 2.5

the surface of the films is more homogeneous than that of at low pH. The surface morphology is seen to be influenced by the electrolyte pH. The change of the surface morphology with the electrolyte pH may be explained by the hydrogen evolution occurred at the cathode surface. Many studies show that electrochemical conditions such as electrolyte pH and deposition potential affect the structure and/or morphology of the films [9, 11, 12] that are in good agreement with the surface morphology findings in this study.

A magnetic field up to 20 kOe was applied both parallel and perpendicular to the film plane. The low-field hysteresis loops of the films are shown in Fig. 4(a) and the high-field loops are represented in Fig. 4(b). The results of magnetic measurements are presented in Table 1. It can be seen that in-plane hysteresis loops have higher remanent magnetization and lower saturation field than the perpendicular loops indicating the easy axis direction is parallel to the film plane.

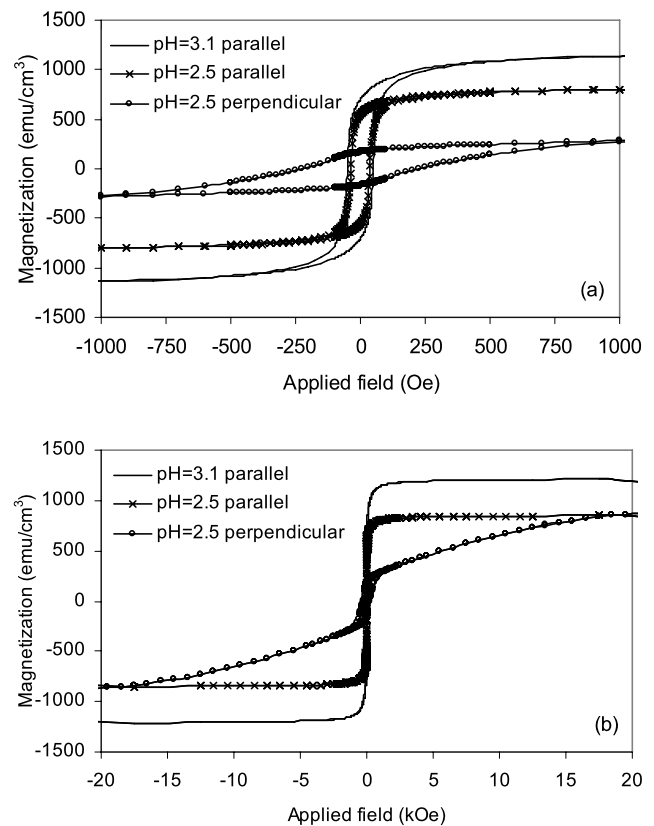


Fig. 4 Parallel and perpendicular (a) low-field and (b) high-field hysteresis loops of Co films at pH = 3.1 and pH = 2.5

Saturation magnetization, M_s decreases from 1201 emu/cm^3 to 840 emu/cm^3 as the electrolyte pH decreases. This may come from the change of crystal structure of Co films deposited at high and low pH. Coercivity, H_c decreases from 49 Oe to 35 Oe and squareness (M_r/M_s) increases with the decrease of electrolyte pH from 3.1 to 2.5. The decrease of grain size from 70 nm (for high pH) to 48 nm (for low pH) is consistent with the decrease of H_c . The dependence of H_c with the grain size was found to have same trend with other studies [13, 14]. A possible explanation for the reduction of the coercivity may come from the fact that the high-pH sample consists of only hcp grains which have high magnetocrystalline anisotropy whereas in the low-pH sample the presence of fcc-crystallites results in a reduction of the overall magnetocrystalline anisotropy which is the major source of coercivity. As seen in Table 1, the perpendicular coercivity values also decreased from 215 Oe to 179 Oe with the decrease of the grain size.

4 Conclusions

Co films were electrodeposited on Cu substrates potentiostatically. It was observed that the structural properties of the films were affected by the electrolyte pH. Crystal structure

of the film at high pH was hcp whereas it was hcp + fcc mixed phase at low pH. Morphology also changed with the change of electrolyte pH. From the magnetic measurements, it was seen that coercivity decreased as the electrolyte pH decreased. The change of coercivity was also consistent with the change of the grain size of Co films.

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