

The effect of pH on the particle size of electroplated Cobalt

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1. Introduction

The most frequently used techniques for the preparation of ⁵⁷Co Mössbauer sources comprise a deposition of the radioisotope onto the surface of a selected metal matrix followed by thermal diffusion of the deposition into the metal lattice [1-2]. The thermal annealing of different metal matrices (Cu, Au, Fe, Co and Pt) with electrodeposited ⁵⁷Co described by Stephen [3] was performed in a continuously pumped vacuum furnace (10⁻⁴~10⁻⁵ hPa) at temperatures of 950–1100 °C depending on the matrix metal. The annealing time was selected to be between 12 and 50 h. An optimized electro deposition process of carrier-free ⁵⁷Co onto the rhodium foil was described earlier.

⁵⁷Co plating is similar to other electroplating processes that employ soluble metal anodes. Specifically, it requires the passage of direct current (DC) between two electrodes that are immersed in a conductive, aqueous solution of nickel salts. The flow of a DC causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The cobalt in the solution is present in the form of divalent positively charged ions (Co²⁺). When the current flows, the positive ions react with two electrons (2e⁻) and are converted into metallic cobalt (Co⁰) at the cathode surface. The reverse occurs at the anode where metallic nickel is dissolved to form divalent positively charged ions that enter the solution.

Charged Co ions are formed by sulfate, sulfamate, chloride, and a Watts bath [4]. However, charged ⁵⁷Co ions are formed by dissolving metal ⁵⁷Co. To establish the coating conditions for ⁵⁷Co, non-radioactive Co ions are dissolved in an acid solution and electroplated onto a Cu plate.

In the present study, the influence of the pH of the plating solution on the grain size was studied. The proposed model can also be applied for radioactive ⁵⁷Co electroplating.

2. Experimental Technique

Cobalt (Co) coatings were deposited by DC electroplating at current densities of 20 mA/cm². The metal composition in the sulfamate bath was 0.16 M of Co prepared by applied surface concepts (SIFCO). The pH of the bath was adjusted from 1.89 ± 0.2 to 5 ± 0.2 by the drop wise addition of KOH (1N). A copper (Cu) plate of 99.99 % purity with dimensions of 10 × 20 × 0.125 mm³ was used as a cathode (substrate) and a Pt-coated Ti mesh with dimensions of 25 × 135 × 1 mm³ as an anode. The deposition time was adjusted to achieve an average thickness of 6 μm based on

Faraday's law [5]. The microstructure of the coatings was studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). XRD investigations were carried out using a Philips X'Pert-Pro instrument operated at 40 kV and 30 mA with CuKα radiation (k = 1.5418 Å). The average particle size of the nanocrystalline Co coatings was calculated from XRD patterns using the modified Scherrer relationship expressed in [6].

3. Results and discussion

Co deposition was produced at a current density of 20 mA/cm², a bath temperature of 27 °C, and various pH levels from 1.89 to 5. XRD patterns showed that the crystal structure of the coating is pure hcp cobalt, and no characteristic peaks of other phases have been recorded. The crystal orientation of the films was estimated by a degree of high (hcp) Co orientation in the XRD patterns. From the peak broadening of XRD patterns, the average crystalline size calculated from the XRD line broadening of the (101) peak was determined using the classical Scherrer relationship [6], $D(hkl) = k\lambda/B \cos \theta$, where $D(hkl)$ is the particle diameter, k is the constant (shape factor) with a value of 0.9, B is half of the maximum line width, and λ is the wavelength ($\lambda = 1.5418 \text{ \AA}$). The size of the deposited particles was at or below 90 nm. The smallest size of the particles was 23 nm, which was formed at a current density of 20 mA/cm². In the XRD results, the second phase was observed in electroplated samples at and above pH 4, and 5, as shown in Fig 1. Although the second phase was performed during electroplating, the thermal diffusion process should be carried out by annealing under a vacuum and Ar atmosphere. Thus, the second phase will be changed to a metal phase. This should be dealt with in a further study.

Figure 2 shows the results of scanning electron microscopy (SEM) for the electrodeposited Co on a Cu plate at a pH of 1.89, 3, 4, and 5. The deposition was carried out at a current density of 20 mA/cm². The creation of the hole and pitch was observed on the coating layer prepared at and above pH 4. The particle size was decreased, as the pH was increased up to 5. The particle size was measured to be the about 77, 75, 26, and 23 nm, as pH was increased from 1.89, 3, 4, and 5, respectively.

Figure 3 shows the results of magnified images of SEM for the electroplated Co at a pH 1.89, 3, 4, and 5. The deposition was carried out at a current density of 20 mA/cm². The creation of the hole and pitch was observed on the coating layer prepared at and above pH

4. The deposition time was calculated to achieve an average thickness of 3~5 μm based on Faraday's law [5].

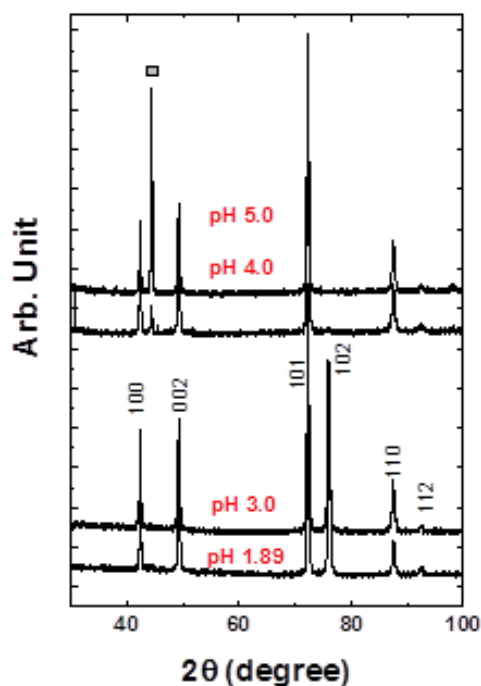


Fig. 1 XRD patterns for electroplated Co on a Cu plate at a different pH of 1.89, 3, 4, and 5.

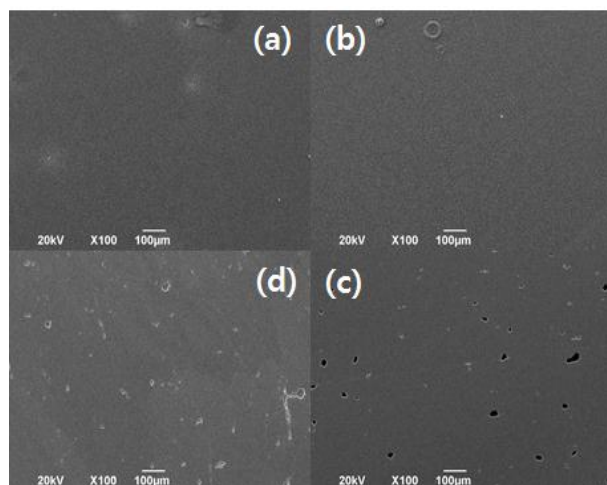


Fig. 2 SEM images for the electrodeposited Co on a Cu plate at a pH 1.89, 3, 4, and 5.

4. Conclusions

For the deposition of Co nanoparticles, nanocrystalline cobalt (Co) coatings were synthesized using DC electrodeposition at a pH of 1.89 to 5 and $20\text{mA}/\text{cm}^2$. The bath was primarily composed of 0.16 M Co ions in a sulfamate bath. The effects of the pH on the average particle size of the deposits were investigated by XRD and SEM techniques. The results showed that the

average grain size decreased to 25 nm as the pH increased to 5. However, the second phase of Co-oxide was formatted, as the pH was increased to and above 4.

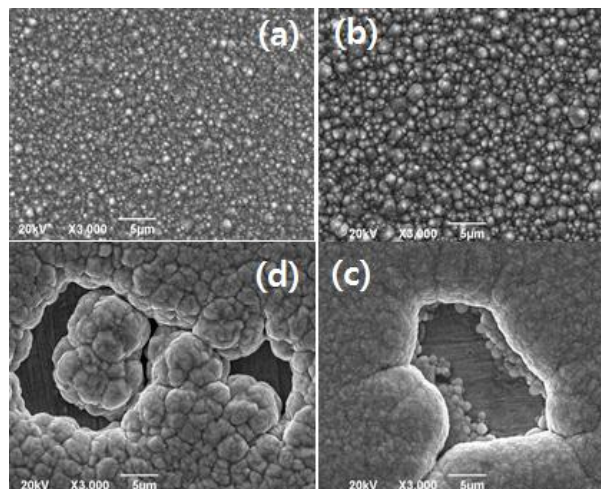


Fig. 3 Magnified SEM images for the electrodeposited Co on a Cu plate at a pH of 1.89, 3, 4, and 5.

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