

COMPARATIVE STUDIES OF MORPHOLOGICAL AND MICROSTRUCTURAL PROPERTIES OF ELECTRODEPOSITED NANOCRYSTALLINE TWO-PHASE Co-Cu THIN FILMS PREPARED AT LOW AND HIGH ELECTROLYTE TEMPERATURES

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In this work, we have studied the effect of the electrolyte temperature on the compositional, structural, and morphological properties of the Co-Cu thin films grown onto ITO coated glass substrates by galvanostatic electrodeposition. The galvanostatic potential-time transients were employed to study the deposition growth process of the films. The compositional analysis which was made using an energy dispersive X-ray spectroscopy (EDX) indicated that the Cu composition in the films enhances with increasing electrolyte temperature. From the X-ray diffraction (XRD) analysis, all of the Co-Cu films were found to consist of hexagonal close-packed (HCP) Co and face-centered cubic (FCC) Cu phase structures regardless of electrolyte temperature. The peak intensities were also changed with electrolyte temperature. It was observed that an enhancement in the electrolyte temperature gives rise to an increase in the average crystallite size of both Cu and Co particles. Atomic force microscopy (AFM) analysis revealed that temperature of the electrolyte significantly affects the surface morphology of the films. Here, several surface roughness parameters such as root mean square (RMS) roughness, average roughness, maximum peak height, and maximum valley depth were also presented as a function of the electrolyte temperature.

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1. Introduction

The properties of Co-Cu films grown at different deposition conditions by electrochemical deposition method have been intensively studied for a long time because of their potential applications in many industrial areas [1, 2]. Electrodeposition has been considered as a feasible alternative technique to the expensive vacuum techniques for preparation of magnetic multilayers and nanocrystalline alloy thin films due to the distinct properties such as simplicity, inexpensiveness, easy scale up, possibility to grow films on irregular surfaces, and relatively high deposition rate [3-11]. It is well known that the microstructural and morphological properties of the films significantly change with the electroplating parameters. Among them, as an important electroplating parameter, the electrolyte temperature in deposition process has a significant effect on the properties of electrodeposited films. However, only a few studies have been carried out on the properties of electrodeposited Co-Cu films prepared at different electrolyte temperatures [12, 13]. To our knowledge, particularly, the analysis of the morphological properties of the electrodeposited two-phase Co-Cu films prepared onto ITO coated glass substrates with respect to electrolyte temperature using AFM has not been reported up to now. The electrolyte temperature is known as one of the most important deposition parameters, because it influences the physical and mechanical properties of electrodeposited thin films such as chemical composition, grain size, texture, and surface roughness, etc. [14]. Therefore, in the present work, the aim is to obtain the Co-Cu films by electrochemical deposition method at various electrolyte temperatures and investigate its effect on the morphological and microstructural properties of the films. Here, it was

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shown that the investigated properties of the electrodeposited Co-Cu films are significantly affected by the temperature of the electrolyte.

2. Experimental

Co-Cu films were electrodeposited onto ITO coated glass substrates under potentiostatic control using VersaSTAT 3 model potentiostat/galvanostat in a three-electrode electrochemical cell. A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and counter electrode (anode), respectively. ITO coated glass substrates were served as working electrode. The working area was about 0.64 cm^2 . Deposits were prepared from freshly prepared electrolytes comprising of Co sulfate, Cu sulfate, and boric acid with concentration of 0.3 M, 0.03 M, and 0.2 M, respectively. All chemicals were dissolved in deionized water. The electrolyte pH was 4.5 ± 0.1 . In this study, three different electrolyte temperatures such as 25°C , 35°C , and $45 \pm 2^\circ\text{C}$ were chosen for the investigation of its effect on the film properties. The ITO coated glass substrates were cleaned in acetone for 5 min and then in ethanol for 5 min. Then, they ultrasonically cleaned with deionized water for 10 min before electrodeposition of the films onto it. Cleaned ITO coated glass substrate was mounted on a working electrode. In all deposition processes, the films were prepared at a constant current of -25 mA and the electroplating time was adjusted to obtain the Co-Cu films with thickness of around 500 nm using the Faraday's law. The structure of the samples was investigated by Panalytical-Empyrean XRD diffractometer using $\text{CuK}\alpha$ radiation ($\lambda=0.154059 \text{ nm}$). The XRD data were recorded in a range from 42° to 54° with a step width of 0.05° . The average crystallite size was determined according to the XRD peak broadening using the Scherrer formula with respect to electrolyte temperature. The surface morphology and surface roughness values of the prepared Co-Cu films was determined using an AFM (Veeco Multimode 5) in tapping mode. AFM images of the films were further processed and analyzed using the WSxM software (Version 4.0) [15], which includes the determination of surface roughness parameters such as maximum peak height and maximum valley depth. The chemical composition of the films as a function of electrolyte temperature was determined by means of energy dispersive X-ray spectroscopy (EDX).

3. Results and Discussion

In the present study, the effect of electrolyte temperature on the chemical composition, morphological, and microstructural properties of two-phase Co-Cu films were studied. The galvanostatic potential-time transients were first employed as a function of electroplating time during the deposition process in order to study the deposition growth process of the films. Figure 1 shows the galvanostatic potential-time transients of the films prepared from the electrolytes with different temperatures recorded for the first 20 s of electroplating process. The effect of electrolyte temperature on the deposition process of Co-Cu films is clearly seen from Fig. 1. The cathode potential increases towards more positive values as the temperature of the electrolyte increases. This may be ascribed to the change in the amount of cupric species occurred at the cathode surface depending on the electrolyte temperature. It has been shown that an enhancement in electrolyte temperature favors the diffusion of cupric species [16]. Therefore, at higher electrolyte temperatures, the diffusion of cupric species is more pronounced and it may affect the deposition growth process of the films.

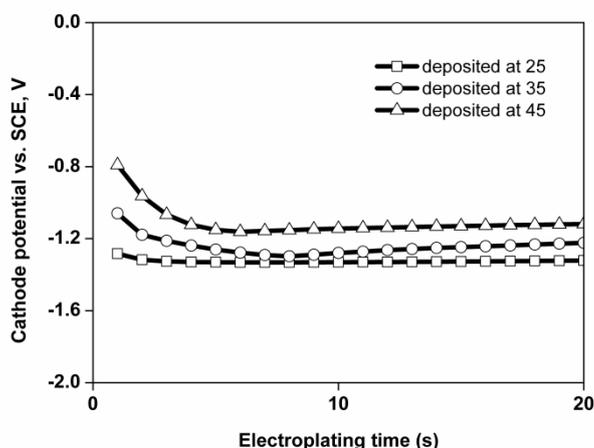


Fig. 1. Galvanostatic potential-time transients of the electrodeposited Co-Cu thin films in the first 20 s

The chemical composition of the films was investigated using EDX with respect to electrolyte temperature. Fig. 2 shows the dependence of the film composition on the temperature of the electrolyte. It is clearly seen from Fig. 2 that the Cu content within the films increases with increasing electrolyte temperature. As shown from Fig. 1, an increase in the cathode potential towards more positive values with rising electrolyte temperature leads to the formation of the Co-Cu films with higher Cu content at higher electrolyte temperatures. It is well known that the Co-Cu films are copper-rich as the films were electrodeposited at more positive deposition potentials [17]. An increase in the Cu content of Co-Cu, Fe-Cu, and Ni-Cu films with increasing electrolyte temperature was also observed in previous studies [12, 13, 16-19], supporting our results found in the present study. Accordingly, it is concluded that the electrolyte temperature strongly affects the chemical composition of the films and as a result of this the morphological and microstructural properties of the films are also considerably affected by the electrolyte temperature.

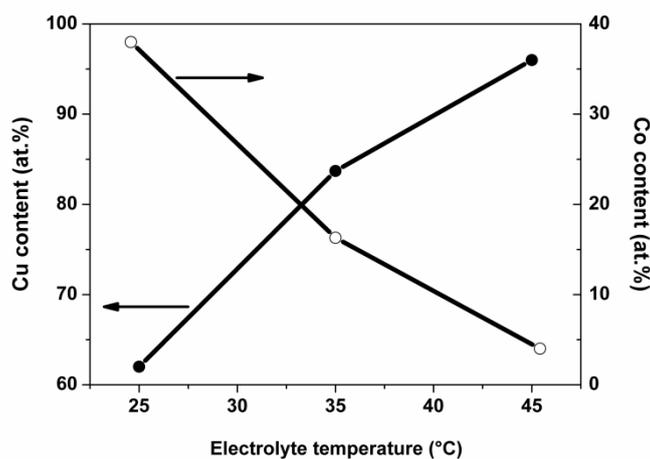


Fig. 2. The evolution of the Cu and Co contents within the Co-Cu films as a function of electrolyte temperature

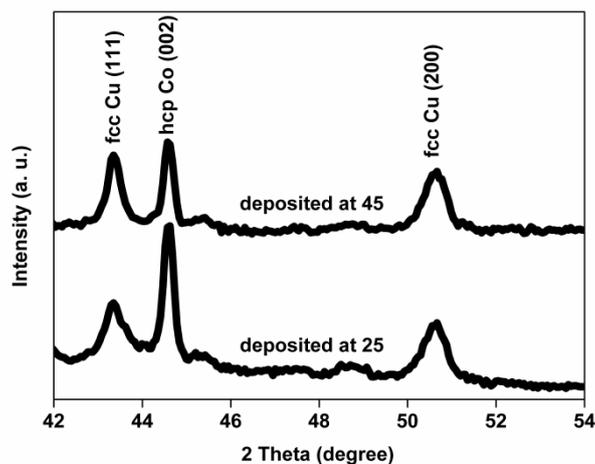


Fig. 3. XRD patterns of electrodeposited Co-Cu thin films grown at low and high electrolyte temperatures

The phase structure of the electrodeposited Co-Cu films prepared at various electrolyte temperatures was characterized by means of X-ray diffraction analysis. The XRD patterns of the electrodeposited Co-Cu films grown at low and high electrolyte temperatures are shown in Fig. 3. From the XRD patterns it is clearly seen that the films electrodeposited at different electrolyte temperatures are polycrystalline. From the XRD patterns, it is observed that the (111) and (200) reflection peaks of the FCC copper appear at the angular positions of around $2\theta=43.36^\circ$ and 50.60° , respectively. Besides, the reflection peak appeared at the angular position of around $2\theta=44.6^\circ$ corresponds to the (002) reflection of the HCP cobalt. Consequently, the XRD patterns given in Fig. 3 suggest that the Co-Cu films consist of HCP Co and FCC Cu phase structures with the lattice parameters close to the corresponding pure phases (HCP Co=0.20303 nm and FCC Cu=0.20871 nm [20]) as observed in previous published studies [2, 17]. Furthermore, it is clearly seen that the peak intensities of the FCC Cu (111) and HCP Co (002) phase structure vary with the electrolyte temperature. The intensity of Cu (111) peak of the FCC phase structure becomes stronger, whereas the intensity of Co (002) peak of the HCP phase structure becomes weaker with increasing electrolyte temperature. This phenomenon may be ascribed to the enhancement in the Cu content of the films with rising electrolyte temperature as shown from the EDX data given in Fig. 2.

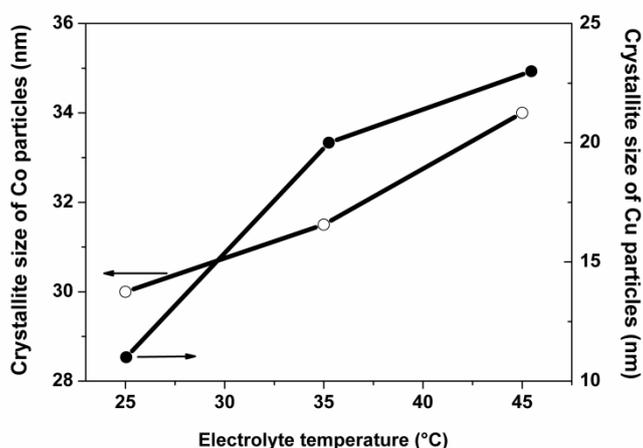


Fig. 4. The average crystallite sizes of Cu and Co particles with respect to electrolyte temperature

The average crystallite sizes of the films as a function of electrolyte temperature are also determined from the peak broadening of the FCC Cu (111) and HCP Co (002) phase structures using Scherrer equation [21]. The average crystallite size of the films with respect to electrolyte temperature is shown in Fig. 4. The average crystallite size is found to be in the range from 34 to 11 nm, indicating that all of the films electrodeposited at different electrolyte temperatures have nanocrystalline structure. As mentioned above, since the cathode potential increases towards more positive values with increasing electrolyte temperature (see Fig. 1), it is expected that the average crystallite size of the films increases with the electrolyte temperature. It is clearly seen from Fig. 4 that an increase in the electrolyte temperature gives rise to an enhancement of the average crystallite sizes of both Cu and Co particles. However, the crystallite size of Cu particles increases more rapidly compared with that of Co particles. The average crystallite sizes of Co particles increase only from 30 to 34 nm, while the average crystallite sizes of Cu particles increase from 11 to 23 nm as the electrolyte temperature increases. And also, the average calculated crystallite sizes of Cu particles are found to be lower than that of Co particles regardless of electrolyte temperature as shown from Fig. 4. These results which were found in the present work are different from the results of that study [2]. These differences may be attributed to the different electroplating conditions such as electrolyte composition, thickness, electrolyte pH, and/or substrate [2].

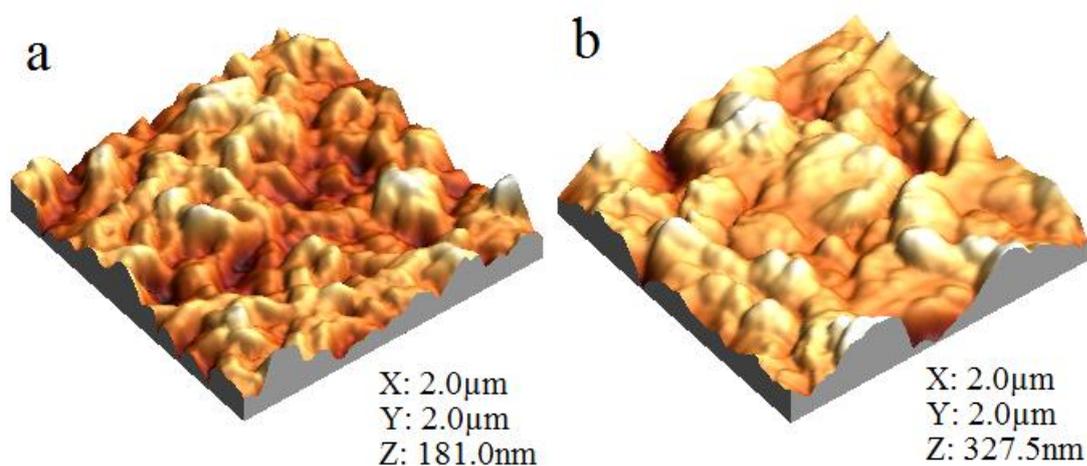


Fig. 5. Three-dimensional AFM topographic images of the Co-Cu thin films electrodeposited at different electrolyte temperatures a) 25 °C and b) 45 °C, respectively

The influence of electrolyte temperature on the surface morphological structure was investigated using the AFM technique. Three-dimensional AFM images of the films electrodeposited at low and high electrolyte temperatures recorded over a scan area of $2\ \mu\text{m} \times 2\ \mu\text{m}$ are shown in Fig. 5a and b, respectively. AFM images show a granular structure for the electrodeposited two-phase Co-Cu films irrespective of electrolyte temperature. The AFM images indicate that the size of particles increases and the number of them decreases as the electrolyte temperature enhances, which implies that less nucleation sites form on the ITO coated glass substrate. In addition to that, it is clearly seen from the AFM images that the smaller particles agglomerate together to form bigger particles. From Fig. 1, it is observed that the cathode potential increases towards more positive values with rising electrolyte temperature. This process may lead to lower nucleation density resulting in the formation of bigger particles.

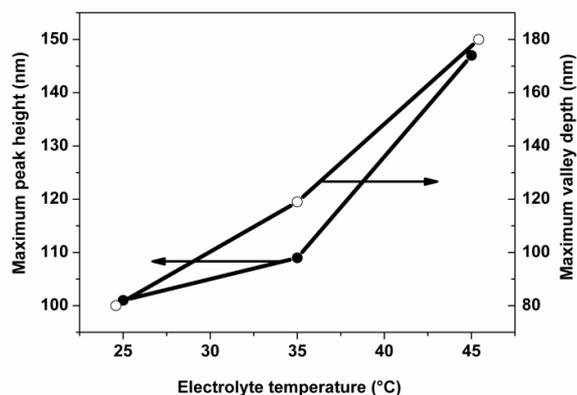


Fig. 6. The evolution of maximum peak height and maximum valley depth values as a function of electrolyte temperature

On the other hand, the surface roughness parameters were determined from the AFM images with the help of the WSxM 4.0 software [15]. The evolution of maximum peak height and maximum valley depth values as a function of electrolyte temperature was shown in Fig. 6. The maximum peak height values are found to be ~101 nm, 109 nm, and 147 nm while the maximum valley depth values are determined to be ~80 nm, 119 nm, and 180 nm for the films electrodeposited from the electrolytes with the electrolyte temperatures of 25 °C, 35 °C, and 45 °C, respectively. It is clearly seen that both of them significantly increase with increasing electrolyte temperature. Moreover, the sum of them also increases with the electrolyte temperature, indicating that the overall roughness of the surface increases [22]. The evolution of the root-mean square (RMS) and average roughness values obtained through the AFM analysis with respect to electrolyte temperature is given in Fig. 7. It is clear that the RMS and average roughness values considerably increase as the electrolyte temperature increases. An enhancement in the surface roughness values can be due to an increase in the particle size observed at higher electrolyte temperatures. Consequently, the results obtained from the AFM analysis clearly revealed that the surface roughness parameters of the electrodeposited two-phase Co-Cu films are considerably affected by the electrolyte temperature.

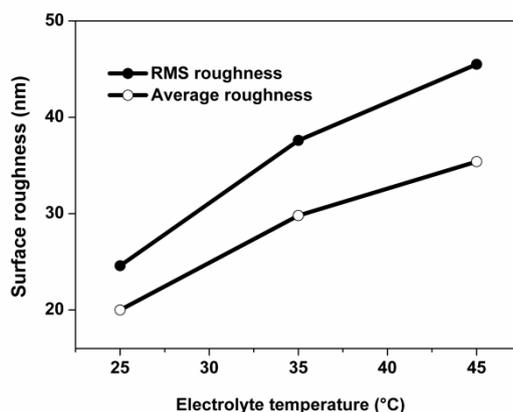


Fig. 7. Surface roughness values as a function of electrolyte temperature

4. Conclusion

Here, a study has been performed about the effect of electrolyte temperature on the microstructural, compositional, and morphological properties of electrodeposited Co-Cu films grown onto ITO coated glass substrates under galvanostatic conditions. A change in the electrolyte temperature is found to have a significant effect on the studied properties of electrodeposited Co-Cu films. From the potential-time transients of the films, the cathode potential is observed to increase

towards more positive values with rising electrolyte temperature. Electrodeposited Co-Cu films are found to compose of HCP Co and FCC Cu phase structures. The intensity of the Cu (111) peak of the FCC phase structure increases, while the intensity of the Co (002) peak of the HCP phase structure decreases as the temperature of the electrolyte increases possibly due to the increase of Cu content within the Co-Cu films with rising electrolyte temperature. The average crystallite size of both Co and Cu particles increases with the increase of the electrolyte temperature. The maximum peak height and maximum valley depth values are found to increase with rising electrolyte temperature. It is also observed that an increment in the electrolyte temperature gives rise to an increase of the particle size and surface roughness. At different electrolyte temperatures, it is observed that the microstructural and morphological properties of the films are different and this may be due to the compositional changes. As a result, it can be reported that the compositional, morphological, and microstructural properties of the electrodeposited two-phase Co-Cu films grown onto ITO coated glass substrates are affected significantly by the temperature of the electrolyte used for the preparation of them.

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