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Differences observed in the surface morphology and microstructure of Ni-Fe-Cu ternary thin films electrochemically deposited at low and high applied current densities

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Abstract. In this research, nanocrystalline Ni-Fe-Cu ternary thin films using electrochemical deposition technique were produced at low and high applied current densities onto Indium Tin Oxide (ITO) coated conducting glass substrates. Change of surface morphology and microstructural properties of the films were investigated. Energy dispersive X-ray spectroscopy (EDX) measurements showed that the Ni-Fe-Cu ternary thin films exhibit anomalous codeposition behaviour during the electrochemical deposition process. From the X-ray diffraction (XRD) analyses, it was revealed that there are two segregated phases such as Cu-rich and Ni-rich within the films. The crystallographic structure of the films was face-centered cubic (FCC). It was also observed that the film has lower lattice micro-strain and higher texture degree at high applied current density. Scanning electron microscopy (SEM) studies revealed that the films have rounded shape particles on the base part and cauliflower-like structures on the upper part. The film electrodeposited at high current density had considerably smaller rounded shape particles and cauliflower-like structures. From the atomic force microscopy (AFM) analyses, it was shown that the film deposited at high current density has smaller particle size and surface roughness than the film grown at low current density.

1. Introduction

Ni-Fe-Cu system has attractive properties such as low coercivity and high conductivity, therefore much attention has been paid both technologically and scientifically for the investigation of their properties [1–3]. It has been reported that the optimal compositions of the Ni-Fe-Cu thin films used for production of magnetic sensors include Ni between 45% - 80%, Fe between 5% - 20%, and Cu between 10% - 50% [4, 5]. There are different production methods of preparing such magnetic thin films. Among them, electrodeposition method has attracted significant attention for a long time in fabricating magnetic thin films owing to their unique advantages. However, it is well known that many electroplating conditions strongly affect the surface morphology and structural properties as well as magnetic properties of the electrochemically deposited magnetic thin films.

In this study, the differences observed in the microstructural and morphological properties of the electrochemically deposited Ni-Fe-Cu ternary thin films with respect to applied current density were presented and discussed. From the analyses, especially, it was revealed that a change in the current density applied during the electroplating process significantly affects the surface morphology and the

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texture degree of Ni-Fe-Cu ternary thin films grown onto ITO coated glass substrates by electrochemical deposition technique.

2. Experimental

Ni-Fe-Cu ternary thin films were electrochemically deposited from an electrolyte solution containing 0.07 M Ni sulfate, 0.004 M Cu sulfate, 0.05 M boric acid, and 0.008 M Fe sulfate at different applied current densities. Deionized water was used to prepare all of the electrolyte solutions. The electrolyte solutions used for the electrochemically deposition of Ni-Fe-Cu magnetic ternary thin films were freshly prepared before each deposition process. It was determined that the pH value and the temperature of freshly prepared electrolyte solutions were 4.2 ± 0.1 and 25 ± 1 °C, respectively. All electrochemical deposition experiments were carried out in a conventional three-electrode cell consisting of counter, working, and reference electrodes using a potentiostat/galvanostat (VersaSTAT 3). A platinum wire, ITO coated conducting glass substrates with a working area of about 1 cm^2 and a saturated calomel electrode (SCE) were served as the counter electrode, working electrode, and reference electrode, respectively. The films were prepared at different applied current densities such as low (-12 mA/cm^2) and high (-20 mA/cm^2) at ambient temperature and pressure without stirring. Before electrochemically deposition process, the surface of the substrates was cleaned in the medium for 5 min in acetone followed by 5 min in ethanol and finally rinsed ultrasonically in deionized water for 10 min. The film thickness was controlled by charge and it was kept constant at 500 nm by adjusting the electroplating time based on the Faraday's law for all applied current densities.

In order to obtain the crystal structure of the films, XRD measurements were performed with a Panalytical Empyrean XRD diffractometer (Cu Kα radiation, λ=0,154059 nm) by scanning in the 2θ=42°-54° range with 0.02 steps. The compositional analysis of the films was done by EDX consisted in the SEM. In order to investigate the effect of applied current density on the surface morphological structure of the films a SEM (Zeiss Supra 50Vp) and an AFM (Veeco, Multimode 5) were used.

3. Results and Discussion

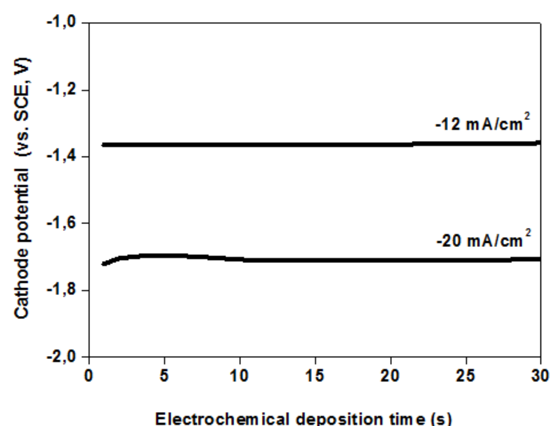

Figure 1. Galvanostatic potential–time transient curves of electrochemically deposited Ni-Fe-Cu ternary thin films with respect to applied current density.

In the present study, the morphological and microstructural properties of Ni-Fe-Cu ternary thin films electrochemically deposited at different applied current densities have been investigated. As a first step of this investigation, the galvanostatic potential–time transient curves are recorded with respect to electrochemical deposition time during the experiments. The galvanostatic potential-time transient curves recorded for the first 30 s of electrochemical deposition process as a function of applied current density are shown in Figure 1. It is observed that the cathode potential remains almost stable at each applied current density, reflecting that the Ni-Fe-Cu ternary thin films investigated in the present study can be produced properly onto ITO coated conducting glass substrates during the electrochemical deposition process. Furthermore, the cathode potential increases when the applied current density increases as seen from Figure 1.

From the compositional analyses carried out for the Ni-Fe-Cu ternary thin films grown at low (-12 mA/cm^2) and high (-20 mA/cm^2) current densities, the elements other than Ni, Fe, and Cu are also detected from the energy dispersion X-ray spectrometer (EDS) spectra shown in Figure 2. It is concluded that these detected elements (O, Si, In, Ca, and Sn) arise from the well-known ITO coated conducting glass substrates. However, we have only obtained the atomic percentages of Ni, Fe, and Cu within the films. In the analyses of the EDS spectra, same method was also carried out in our previous research [6] and the other earlier studies [7, 8]. The results obtained from the EDX analyses are showed that the film has 77 at.% Ni, 12.2 at.% Fe, and 10.8 at.% Cu at low applied current density, whereas the chemical composition of the film electrochemically deposited at high applied current density is 80 at.% Ni, 9.6 at.% Fe, and 10.4 at.% Cu, indicating that the preferential deposition of Fe is more pronounced at low current density. Therefore, by changing of applied current density, it is possible to prepare the Ni-Fe-Cu ternary thin films with different chemical compositions.

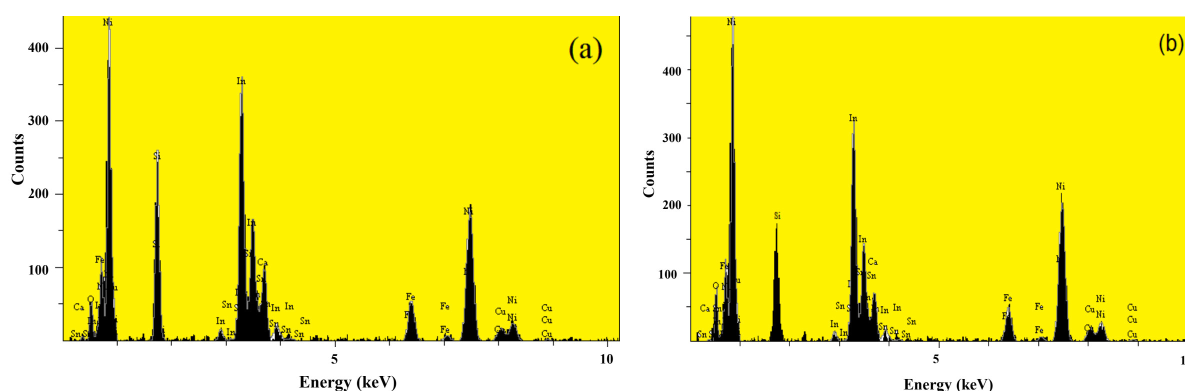

Figure 2. Energy dispersion X–ray spectrometer (EDS) spectra of electrodeposited Ni-Fe-Cu ternary thin films prepared at low and high current densities a) -12 mA/cm^2 and b) -20 mA/cm^2, respectively.

From the results of EDX measurements, there is clear evidence for the existence of anomalous codeposition behavior in Ni-Fe-Cu ternary thin films electrochemically deposited at low and high current densities, since the relative Fe concentration in the films is higher than the relative ion concentration of Fe^{2+} in the electrolyte solution. It was shown that the electrochemically deposited NiFe binary magnetic films prepared onto ITO coated glass substrates exhibit the anomalous codeposition behavior of two iron group elements of Fe and Ni [9]. Furthermore, the anomalous codeposition behavior was also observed in Ni-Cu-Fe ternary thin films electrochemically deposited onto ITO coated glass substrates in our previous study [10].

The XRD patterns revealed the crystallographic structure of the electrochemically deposited Ni-Fe-Cu ternary thin films grown at low and high applied current densities investigated in the present work and ITO coated glass substrate are shown in Figure 3. From the XRD patterns, the (111) and (200) diffraction peaks appeared at the angular positions of around 44˚ and 51˚, respectively, which correspond to FCC structure, are clearly seen. However, the films exhibit two segregated peaks at the angular positions of around 44˚ and also 51˚. According to the results obtained from the XRD analysis, the films are not single-phase. In agreement with previous reports [6, 10-16], we have been also find a phase separation consisting of Cu-rich and Ni-rich phases in electrodeposited Ni-Fe-Cu ternary thin films investigated in the present study. Besides, from the XRD patterns, a shift in the Ni-rich (111) and (200) peak positions towards higher 2θ angles is observed with increasing applied current density, implying that the lattice parameters of the Ni-rich (111) and (200) phases decrease. The lattice parameters of the Ni-rich (111) phase are found to be 0.3532 nm and 0.3526 nm for low and high applied current densities, respectively. These results are also in good agreement with those reported for the Ni-Fe films [17, 18] and Ni-Cu-Fe films [10] which have FCC crystallographic structure.

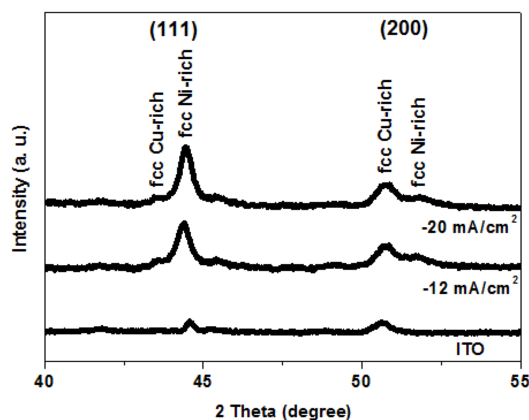

Figure 3. XRD patterns of electrochemically deposited Ni-Fe-Cu ternary thin films prepared at low and high current densities and ITO coated glass substrate.

The average crystallite sizes of the films are determined using a well-known Scherrer formula [19]. All of the films are found to have nanocrystalline structure and the average crystallite size is determined as 14.6 nm at low current density (-12 mA/cm^2) and it is 16.4 nm at high current density (-20 mA/cm^2), indicating that the crystallite size of the films increases with increasing applied current density. As can be seen from Figure 1, since the cathode potential increases as the applied current density increases, it is expected that the average crystallite sizes of the films decrease by increasing the applied current density. However, the variation of the average crystallite size with the applied current density shows an opposite behavior. It has been reported that the average crystallite size increases with increasing applied current density, which has been attributed to the co–deposition of hydrogen at the cathode electrolyte interface [20]. In the existence of hydrogen, the changes in the surface energy and growth mechanisms lead to an increase in the average crystallite size of films by increasing current density [20]. It was also reported in previous studies that an enhancement in the applied current density leads to an increment in the crystallite size, since it reduces the charge transfer resistance and the adsorption intensity of electrochemical active species [21-23].

The lattice micro-strain percentages of the films, ε, were also estimated from the XRD patterns using the following equation [12, 24].

$$\varepsilon = \left(\frac{\beta}{4 \times \mathrm{tg}\theta}\right) \times 100$$

where β represents the full width at half maximum (FWHM) of fcc Ni-rich (111) peak of the films and θ is the Bragg's angle. The lattice micro-strain percentages are found to be 0.62 % and 0.55 % for the films grown at low and high applied current densities, respectively. Thus, it is concluded that an increase in the applied current density induces a lower lattice micro-strain and larger crystallite size.

In order to obtain additional information on the microstructure, the evolution of integral intensities of the Ni-rich (111) and (200) peaks of the films as a function of applied current density are also analyzed by the peak profile fitting of XRD patterns. The integral intensity of the Ni-rich (111) peak increases and the integral intensity of the Ni-rich (200) peak decreases with increasing applied current density, indicating that the relative peak intensity of the Ni-rich (111) phase increases. Thus, we conclude that an increase in the applied current density gives rise to an increment in the texture degree of the Ni-rich (111) phase within the Ni-Fe-Cu ternary thin films.

The morphological structure of the films was investigated using a SEM. Figure 4(a) and (b) show the SEM images of the films electrodeposited at low and high applied current densities, respectively. SEM images revealed that the morphological structure is significantly influenced by the applied current density. As the film is prepared at low applied current density of -12 mA/cm^2, the film surface exhibits a morphology consisting of smaller rounded particles on the base part and larger cauliflower–like structures formed owing to the agglomeration of the smaller rounded particles on the upper part (Figure 4a). The same kind of surface morphology is observed as the film is electrodeposited at high applied current density of -20 mA/cm^2 (Figure 4b). However, the sizes of smaller rounded particles

and larger cauliflower–like structures significantly decrease, while the number of them increases with increasing applied current density.

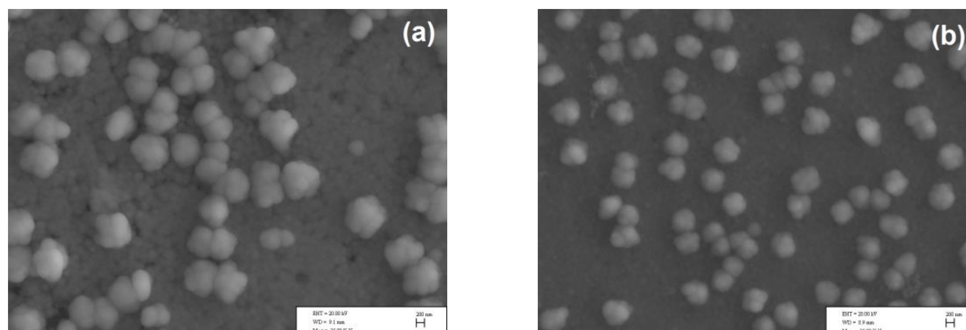

Figure 4. SEM images of the electrochemically deposited Ni-Fe-Cu ternary films grown at low and high current densities a) -12 mA/cm^2 and b) -20 mA/cm^2, respectively.

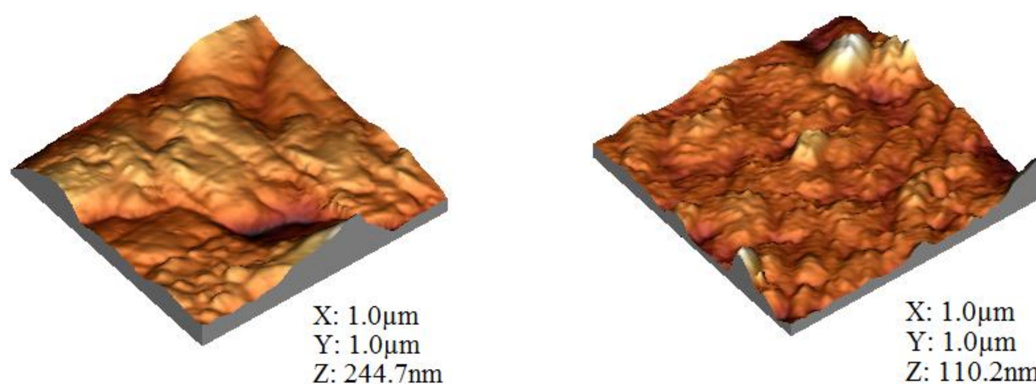

Figure 5. Three dimensional AFM images of the electrochemically deposited Ni-Fe-Cu ternary films produced at low and high current densities a) -12 mA/cm^2 and b) -20 mA/cm^2, respectively.

AFM analyses are also used to investigate of the surface morphology of Ni-Fe-Cu ternary thin films. From the three-dimensional AFM images shown in Figure 5, it is concluded that the surface of the films exhibits granular growth morphology irrespective of applied current density. A decrement in the surface roughness of the films is observed with increasing applied current density. The root mean square (RMS) surface roughness values are found to be 28.2 nm and 12.3 nm for the films grown at low and high applied current densities, respectively. An increase in the nucleation density leads to the formation of smaller particles on the ITO coated glass substrates at high applied current density during the electrochemical deposition process of the films, resulting more compact and smooth film. The differences observed in the particle size and/or surface morphology with the applied current density may be ascribed to the change of chemical composition of the films. It was also shown that the applied current density affects the particle size and/or surface morphology of the electrodeposited metallic thin films in previous studies [25-27].

4. Conclusions

We have been investigated the effect of applied current density on the crystallographic structure, crystallite size, texture degree, lattice strain, surface roughness, and grain size of electrochemically deposited Ni-Fe-Cu ternary thin films prepared onto ITO coated conducting glass substrates. Compositional analyses indicated that the Ni-Fe-Cu ternary thin films have the composition of 77-80 at.% Ni, 9.6-12.2 at.% Fe, and 10.4-10.8 at.% Cu. Electrochemically deposited Ni-Fe-Cu ternary thin

films exhibit anomalous codeposition behavior irrespective of applied current density. The XRD analyses show that the Ni-Fe-Cu ternary thin films have two segregated Ni-rich and Cu-rich phases. Ni-Fe-Cu ternary thin films investigated in the present study are found to have FCC crystal structure. The film has larger crystallite size and lower lattice micro-strain at high applied current density. An increment in the applied current density induces an enhancement in the texture degree of Ni-rich (111) phase within the Ni-Fe-Cu ternary thin films. The films exhibit a morphology having of smaller rounded particles on the base part and larger cauliflower–like structures on the upper part regardless of applied current density. The film electrochemically deposited at high current density has smaller particles compared to those grown at low current density. The RMS surface roughness and particle size decrease when the film is electrochemically deposited at high current density. The differences observed in the properties of the films can be attributed to the change of the film composition affected by the applied current density.

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