AENSI Journals

JOURNAL OF APPLIED SCIENCE AND AGRICULTURE

ISSN 1816-9112

Journal home page: www.aensiweb.com/JASA

Electrodeposition of CoNiFe alloy thin films in a sulfate solution

Ismail Hanafi, Abdul RazakDaud, ShahidanRadiman

[1]*School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43500 Bangi, Selangor Malaysia.*

ARTICLE INFO

Article history:
Received 31 December 2014
Received in revised form 26 January 2015
Accepted 28 January 2015
Available online 11 February 2015

Keywords:
Potentiostatic Sulfate salt
Ferromagnetic

ABSTRACT

The aim of this study was to synthesize the ternary CoNiFe alloy thin films by electrodeposition technique at different potentials in a sulfate solution. The CoNiFe alloy thin films were electrodeposited on indium tin oxide (ITO) substrate. Voltammetric studies indicated potential region for deposition of cobalt, nickel and iron lied in range of -1.10 V to -1.30 V. The energy dispersive X-ray (EDX) analysis indicated that Ni content of the films significantly increased, whereas the Co and Fe content decreased as the electrodeposition potentials were made more negative values. The scanning electron microscopy (SEM) study showed the electrodeposition occurred uniformly. Hysteresis curves of the ternary alloy film obtained from vibrating sample magnetometer results proved to be ferromagnetic.

ToCite ThisArticle: Ismail Hanafi, Abdul RazakDaud, ShahidanRadiman, Electrodeposition of CoNiFe alloy thin films in a sulfate solution. ***J. Appl. Sci. & Agric.,*** *10(5): 58-62, 2015*

INTRODUCTION

Magnetic films of Co, Ni and Fe have attracted attention to many researchers(Su & Qiang 2012; Sundaram *et al*. 2011a; Sundaram *et al*. 2011b) because of their potential applications in reading or writing heads, magnetosensors and magnetic data storage devices(Schwarzacher & Lashmore 1996). In the last few years, intensive studies (Budi *et al*. 2010; Daud *et al*. 2011; Kim *et al*. 2003) have been done on these materials to explore their unique soft magnetic properties. Up to date, computer read/write heads have been manufactured individually by physical deposition technique for giant magnetoresistance (GMR) spin valve read heads and electrodeposition for write heads(Kim *et al*. 2003). The well-known iron group alloy thin film applications are in magnetic thin film recording heads (Andricacos & Robertson 1998; Chiu *et al*. 1996) and microelectromechanical systems (MEMS) with approximately 1.0 T of magnetic saturation (M_s) and low coercivity (H_c). Nonetheless, new soft magnetic materials with greater performance are desirable due to rapid increase of areal density in computer drives(Andricacos & Robertson 1998; Osaka *et al*. 1998), advanced miniaturization and high capability electromagnetic devices in MEMS(Osaka *et al*. 1998; Rasmussen *et al*. 2001). Numerous Co-Ni and Co-Fe-based ternary alloys comprising Co-Fe-B(Liao), Co-Fe-Cu(Andricacos & Robertson 1998) and Co-Ni-Fe(Liu *et al*. 2000; Nam *et al*. 2001; Osaka *et al*. 1998) have been deliberated as potential candidates. In particular, the ternary Co-Ni-Fe alloys have been well identified as one of the promising systems due to their high magnetic saturation flux density (B_S ~2.0 – 2.1 T) and low coercivity (< 2 Oe)(Osaka *et al*. 1999; Osaka *et al*. 1998).

Over recent years, the fabrication of Co-Ni-Fe ternary alloys thin film is prepared through various techniques such as positive microemulsion(Wen *et al*. 2008) and galvanostatic electrodeposition(Rhen *et al*. 2008). The electrodeposition is a prevalent method among other techniques in producing metallic alloy films(Gong *et al*. 2005; Sziráki *et al*. 2010) as the method is economic(Gurrappa & Binder 2008; Martinez *et al*. 2006) and wide range industrial applicability(Gurrappa & Binder 2008). In electrodeposition method, experimental parameters such as electrodeposition potentials(Azizi *et al*. 2013) and electrolyte condition (composition, temperature, additive and pH) can alter the deposition product properties. In this present study, we intend to produce Co-Ni-Fe alloy thin films via potentiostatic mode at various electrodeposition potentials.

Methodology:

A computer-controlled potentiostat was used as a potential source. A sulfate bath containing 0.15M

Corresponding Author: Ismail Hanafi, School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43500 Bangi, Selangor Malaysia.
6017-5778009; E-mail: ismail.hnf@gmail.com

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$CoSO_4$, 0.2M $NiSO_4$, 0.005M $FeSO_4$ and 0.4M H_3BO_3 buffer solution was used for electrodeposition of Co-Ni-Fe alloy. The solution was adjusted to pH 3 by adding a few drops of H_2SO_4 solution and all investigations were conducted at room temperature (25 ^{0}C). The depositions were conducted in a three-electrode cell comprising a platinum wire as counter electrode, saturated calomel electrode (SCE) as reference electrode and indium-doped tin oxide (ITO) coated on glass as working electrode. The polycrystalline ITO coated on glass has diameter of 1.50 cm and thickness of 0.11 cm was used as samples for electrodeposition. The samples were first degreased in acetone for 10 min by ultrasonication method and rinsed in deionized water. Cyclic voltammetry technique was performed using a computer-controlled potentiostat/galvanostat (Voltalab PGZ402) to determine the electrochemical potential region for deposition of Co, Ni and Fe. The surface morphology of the films was observed under a field emission scanning electron microscope (FESEM, MERLIN Compact). The chemical analysis was done using an energy dispersive x-ray (EDX) analyzer equipped to the FESEM. The phase characterization was performed by means of an X-ray diffractometer (XRD, Bruker AXS model D8 Advance) using a monochromatic Cu $K\alpha_1$ source (λ = 0.154056 nm) scanned between 10^0 and 60^0 with the step size of 0.02^0. The magnetic properties were investigated using vibrating sample magnetometer (VSM, Lake Shore model 7404) at room temperature.

RESULTS AND DISCUSSION

Cyclic voltammetry (CV) was performed to define potential region of the Co, Ni and Fe in electrodeposition process. Figure 1 shows the stabilized cyclic voltammograms for deposition of individual element of Co, Ni and Fe, and Co-Ni-Fe alloy at potential scanning rate of 10 mV/s. The potentials were scanned from -1.30 V to 0.6 V, in positive direction, and then reversed to the starting potential. The CV recorded for a solution containing 0.15M $CoSO_4$ is presented in Figure 1(a). Only one single anodic peak (a_1)was observed around 0.119 V which corresponds to the oxidation of cobalt metal into Co^{2+}. During the reversed scan a cathodic peak (c_1) appeared at -0.875 V which corresponds to the reduction of Co^{2+} into cobalt metal. This was followed by a further increase in current due to reduction of H^+. This result is consistent with a previous study on electrochemical deposition of Co^{2+} onto ITO electrodes in sulfate aqueous solutions(Gómez *et al*. 2001). Figure 1(b) shows the voltammetric curve ofnickel at concentration of 0.2 M where the oxidation peak (a_2) is almost disappeared or hardly detected whereas the reduction peak (c_2) appeared at -0.8 V. A similar observation has been reported by Afshar *et al*.(2003). For individual iron (Fig. 1(c)) at concentration of 0.005 M, the anodic peak (a_3) appeared at a further negative region approximately at -0.489 V compared to theindividual cobalt and nickel. During the reversed scan, it was observed the presence of two reduction peaks, c_3 and c_4. The first peak (c_3) corresponds to the iron reduction from Fe^{2+} into iron metal at value about -0.5 V which is significantly close to the Nernstian value. Further increase of negative potential has resulted in the emergence of peak c_4, which corresponds to the hydrogen ion reduction reaction(Grujicic & Pesic 2004). Figure 1(d) shows the cyclic voltammogram for the solution containing 0.15 M $CoSO_4$, 0.2 M $NiSO_4$ and 0.005 M $FeSO_4$. During the cathodic scan, two cathodic peaks, c_5 and c_6 were observed at -0.139 V and -0.875 V respectively. The cathodic peak c_5 also reported by Zhao(2011) which is characteristic of over potential deposition of Fe onto ITO surfaces. Due to lower Fe^{2+} ions concentration, the deposition is diffusion-limited over a wide potential range from c_5 to c_6 peaks. The difference with the cathodic peak of single component solutions is probably due to the fact that Co and Ni start to deposit onto ITO substrate pre-covered by Fe(Azizi *et al*. 2013).

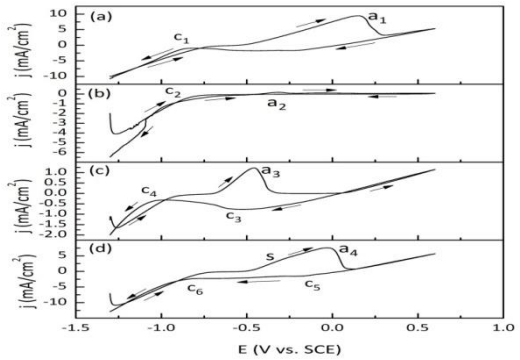

Fig. 1: Cyclic voltammograms of aqueous solution containing 0.4 M H_3BO_3 (pH = 3.0) and (a) 0.15 M $CoSO_4$, (b) 0.2 M $NiSO_4$, (c) 0.005 M $FeSO_4$ and (d) 0.15 M $CoSO_4$ + 0.2 M $NiSO_4$ + 0.005 M $FeSO_4$ at cathodic scan limit = -1.30 V (SCE) and scan rate = 10 mV/s.

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On the anodic scan, a clear anodic peak a_4 with a shoulder is observed. The presence of this shoulder is related to hydrogen dissolution (Mendoza-Huizar *et al*. 2002; Palomar-Pardavé *et al*. 2005). The clear peak of a_4 corresponds to the dissolution of Co-Ni-Fe which was previously deposited during the cathodic scan. This is in good agreement with the work of Gómez *et al*.(2001). The alloy dissolution peak appeared to be in between of its single component dissolution peaks which is not in agreement with the finding by Azizi *et al*.(2013)whom reported the alloy dissolution peak is at more noble potential than those of peaks attributed to Co, Ni and Fe. This is might be due to different in electrolyte composition in the reported literature. Various kinetic factors could be associated with the existence of the alloy peak which cause the peak shifted away from its reversible position in the positive direction(Abd El Rehim *et al*. 2000; Jović *et al*. 1988). It is observed in all curves that the current crossover, and the presence of such hysteresis loop is a featured characteristic of a nucleation and growth progression(Bockris *et al*. 1990).

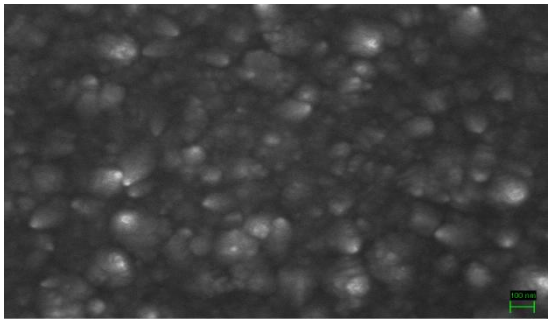

Fig. 2: SEM micrograph of CoNiFe alloy thin film deposited at -1.30 V

The SEM micrograph of the Co-Ni-Fe alloy electrodeposited at -1.30 V (Fig.2) clearly indicates that the electrodeposition occurred uniformly. The existence of Co, Ni and Fe peaks for the electropotential of -1.30 V (SCE) confirmed the fact that the synthesized product is Co-Ni-Fe alloys for the namely potential as showed in EDX spectra (Fig. 3).Analysis of the thin films composition(Fig. 4) show that the Co and Fe content of the alloy decreased with the increase in electrodeposition potentials whereas the Ni content increased.

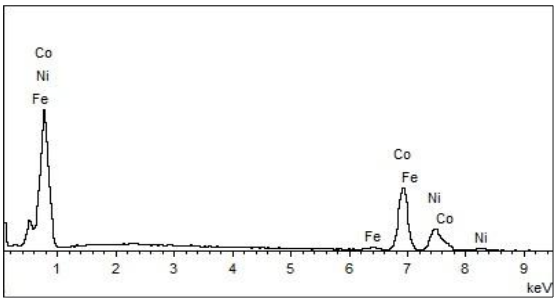

Fig. 3: EDX spectra of CoNiFe alloy thin film deposited at -1.30 V

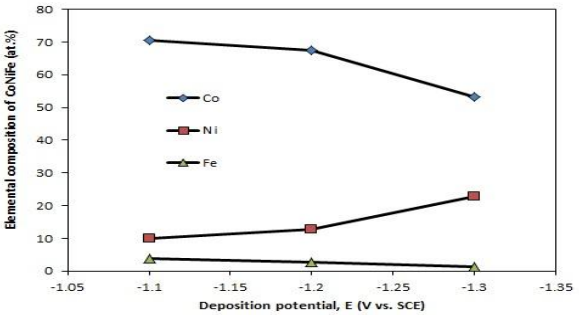

Fig. 4: Elemental composition of CoNiFe alloy thin films deposited at different potentials

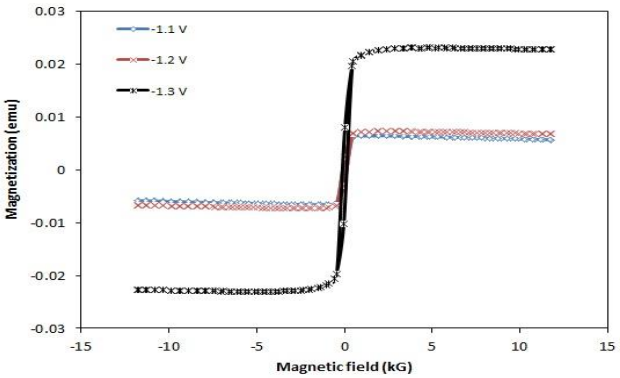

Fig. 5: Hysteresis loops of CoNiFe alloy thin films electrodeposited at different potentials

Typical room temperature hysteresis curves of the alloy are shown in Figure 5 with magnetic field up to 12 kOe. The magnetic hysteresis curves revealed the existence of ferromagnetic phases. It can be seen that the saturation magnetization (M_s) increased from approximately 653 A/m to 2307 A/m as the electrodeposition potentials were increased from -1.10 V to -1.30 V. The coercivity (H_c) values changed slightly between 100 Oe and 118 Oe from the lower potential, -1.10 V to the higher potential, -1.30 V. Based on the composition of the alloy film (Fig. 4), the increase in $M_s$may be due to the decrease in Fe content where Fe has lower M_s value than Ni(Su & Qiang 2012). The change in H_c values might be due to the effect of higher content of Co which led to a slight increase in H_c. Previous finding(Kim *et al*. 2003) reported the $H_c$from sulfate medium was independent of Fe content in the deposit.

Conclusion:

Ternary alloy of Co-Ni-Fe thin film was successfully co-deposited on ITO by potentiostatic electrodeposition method. The thin films were uniform and contained equally sized Co-Ni-Fe alloy particles. The magnetic saturation and coercivity of the film were greatly influenced by electrodeposition potential which influenced the elemental composition of the ternary alloy particles.

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