SENSOR LETTERS
Vol. 7, 1–4, 2009

The Role of Cu Content on Properties of Electrodeposited Fe-Cu Films

Ali Karpuz[1], Mursel Alper[2], and Hakan Kockar[1,*]

[1] Physics Department, Science and Literature Faculty, Balikesir University, Balikesir, Turkey
[2] Physics Department, Science and Literature Faculty, Uludag University, Bursa, Turkey

(Received: 25 February 2008. Accepted: 22 February 2009)

The microstructural and magnetic properties of Fe-Cu films were studied in terms of Cu content in the films. The results of energy dispersive X-ray spectroscopy showed that the Cu content in the films increases as the Cu concentration in the electrolyte is increased. The increase of the Cu content in the films makes the film morphology seem cauliflower-like structure and the films with Cu have rougher surface than pure Fe films. The X-ray diffraction revealed that the films have body-centered cubic structure of α-Fe, and the Fe film has the (100) preferential texture whereas the Fe-Cu film containing 9.5 wt% Cu has the (110) preferential texture. The magnetic analysis carried out by vibrating sample magnetometer showed that the increase of the Cu content in the film results in the decrease of the saturation magnetization and the increase of the coercivity, and the easy-axis direction of the magnetization is parallel to the film plane. It is seen that the microstructural and magnetic properties of the Fe-Cu films changes depending on the film content.

Keywords: Electrodeposition, Fe Films, Fe-Cu Alloys, Magnetic Films.

RESEARCH ARTICLE

1. INTRODUCTION

In the recent years, magnetic films have become focus of comprehensive investigations. This is due to meeting all of the requirements of data storage technology and their potential applications in sensors and actuators. Electroplating has been a process of major significance in the production of magnetic films, which are important in computer drivers and other magnetic storage devices. Electrodeposition, compared to vacuum processes, offers some advantages to produce magnetic materials and has also proved to be a useful technique for preparation of certain kinds of alloys and superlattices.[1–5]

Compositional and Structural properties of the films are known to be highly dependent on the production methods.[4] For Fe-Cu films, high Fe concentration leads to a bcc phase and a low Fe concentration to an fcc phase. However, the phase may be mixed bcc and fcc phase depending on Fe content in films. This case appears at 27–30% Fe for films made by electrodeposition.[4,6] Also, the deposition parameters have a major effect on the properties of the films produced by the electrodeposition. One of these parameters is the concentration of the electrolyte, which considerably affects the film content. Therefore, the aim of the present study is to investigate the effect of Cu content on the microstructure and magnetic properties of the Fe-Cu films. The films were deposited on polycrystalline Ti (hcp) substrate by the electrodeposition technique and their structural and magnetic properties were studied. It is revealed that the properties of the films are influenced by the composition of the films.

2. EXPERIMENTAL DETAILS

The Fe and the Fe-Cu films with different Cu content were deposited in a three-electrode cell from a sulphate bath using a platinum (Pt) plate as the anode and a titanium (Ti) plate as the cathode. Saturated calomel electrode (SCE) was used to fix the potential between anode and cathode as a reference electrode. The surface area of the anode was chosen more extensive comparing to the cathode, the separation between them was 7 cm. Fe films were electrodeposited from an electrolyte containing $FeSO_4$ (1 M) only, and Fe-Cu films from electrolytes containing $FeSO_4$ (1 M) with $CuSO_4$ (0.01–0.02 M). The pH value of electrolytes was 3.0 ± 0.2. All films were deposited at a cathode potential of -1.8 V with respect to SCE. The nominal thicknesses of the films were fixed at 6 μm. All depositions

*Corresponding author; E-mail: hkockar@balikesir.edu.tr

1546-198X/2009/7/001/004
doi:10.1166/sl.2009.1090

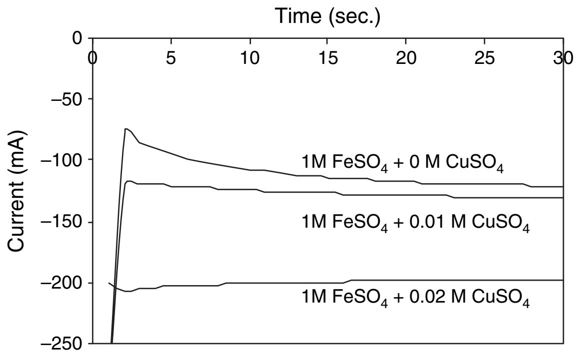

Fig. 1. Current–time transients for Fe and Fe-Cu films deposited from different electrolytes.

were carried out at room temperature (20 ± 1 °C) without stirring of the electrolyte.

Compositional analysis and morphological observations of the films were done by the energy dispersive X-ray spectroscopy (EDX) and the scanning electron microscope (SEM, Zeiss Supra 50 Vp), respectively. The microstructural analysis of the films was made with the X-ray diffraction technique (XRD, Rigaku–rint 2200) using CuK_α radiation ($\lambda = 1.5406$ Å) by changing diffraction angle (2θ) between 40°–100°. The magnetic measurements were made with a vibrating sample magnetometer (VSM, ADE Technologies EV9) by scanning magnetic field between ±20 kOe as parallel and perpendicular to the film plane.

3. RESULTS AND DISCUSSION

Both Fe and Fe-Cu alloy films were electrodeposited on hcp polycrystalline Ti substrates under potentiostatic conditions. Small amount of $CuSO_4$ at each time were added to the $FeSO_4$ electrolyte to deposit the proper Fe-Cu films and comparatively study the properties of Fe and Fe-Cu films. Therefore, three different electrolytes with the proper $CuSO_4$ concentration were prepared for the deposition of the Fe-Cu films.

The current–time transients were recorded to study the deposition processes of the films. Figure 1 illustrates the current–time transients for the Fe and Fe-Cu films. In the figure, as the Cu concentration in the electrolyte is increased from 0 M to 0.01 M and 0.02 M in the order, the cathodic current passed through the electrodes increases. This is most probably caused by the rise of the Cu ions in the electrolyte. Also from current–time transients, it is clearly seen that the films deposited from the electrolytes with different Cu concentrations have the same type of deposition processes and besides understood that films were deposited orderly on the cathode. As expected, a little hydrogen liberation was seen from the cathode surface during the deposition, as in Ref. [7]. All films were slightly spotted and black color in appearance. The study on Fe films[8] indicated that the films grown from the electrolyte containing $FeSO_4$ are also black or dull silver color depending on the experimental parameters.

Compositional measurements showed that Fe-Cu films deposited from the electrolytes (1 M $FeSO_4$ and 0.01 M $CuSO_4$) and (1 M $FeSO_4$ and 0.02 M $CuSO_4$) contain, on average, 3.0 ± 0.1 and 9.5 ± 0.1 wt% Cu, respectively, see Table I. The analysis of surface morphology of the films indicated that the Fe-Cu films have dense dendritic (cauliflower—like) structure, and rougher surface than the pure Fe films as presented in Figures 2(a) and (b). Further, EDX analysis revealed that the Fe-Cu films have Fe rich base part and Cu rich cauliflower-like structure. The reason that affects the surface morphology may be the diffusive growth of Cu occurred in the Fe rich base part. Also in the micrograph of the pure Fe film, there was much smoother surface. As parallel to this, SEM studies of other researchers[9] have also revealed that the films grown from the electrolytes containing two different metal ions have different surface morphology and dendritic structures. According to these results, it was noted that the surface morphology is considerably influenced by the amount of Cu in the film.

To understand the effect of Cu content on the crystal structure of the Fe and the Fe-Cu film containing 9.5 wt% Cu, XRD measurements of the films were done and presented in Figure 3. The results revealed that the peaks appeared on the XRD patterns belong to body-centered cubic (bcc) of α-Fe since our films contain high Fe concentration, as pointed in Ref. [4]. The XRD patterns of

Table I. Microstructural, compositional and magnetic data obtained from XRD, EDX and VSM

	XRD					EDX (wt% ± 0.1)		VSM	
Sample	$CuSO_4$ Content (M)	Lattice Parameter a ± Δa(nm)	Grain size (± 0.1 nm)	Relative Intg. Peak Int. $I_{110}/I_{200}/I_{211}/I_{220}$	P.O.*	Fe	Cu	M_s emu/cm^3	H_c Oe
Fe Film	0.00	0.28656 ± 0.00012	21.9	100/23.2/29.8/4.7	(100)	100	0.0	170.0	19.6
Fe-Cu	0.01	—	—	—	—	97.0	3.0	141.6	23.1
Films	0.02	0.28656 ± 0.00012	25.5	100/7.3/25.5/4.6	(110)	90.5	9.5	122.7	26.3
Bulk Fe**	—	0.2866	—	100/20/30/10	—	—	—	—	—

*Preferential Orientation
**JCPDS 006-0696 XRD data for Fe

RESEARCH ARTICLE

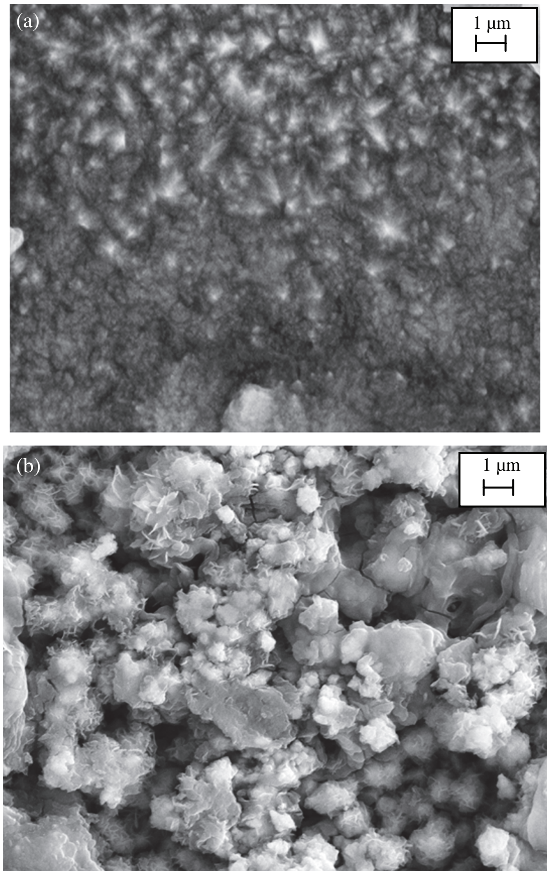

Fig. 2. SEM images of the electrodeposited films (a) The pure Fe film (b) The Fe-Cu film containing 9.5 wt% Cu and 90.5 wt% Fe.

Fe-Cu films do not contain the reflections from the planes of face-centered cubic of Cu phase, which indicates that Fe-Cu films under study form a solid solution. The data of X-ray diffraction patterns were also used to calculate the lattice parameters, the grain sizes and the film textures for Fe film and Fe-Cu film containing 9.5 wt% Cu. The lattice parameter which calculated using the least squares technique to fit experimental data to a straight line was found to be 0.28656 (±0.00012) nm. Although there is a slightly difference between the lattice parameters, it is in the error limits. The grain sizes were calculated from the Scherrer formula[10] using the full width at half maxima (FWHM) of the observed peaks. They were noted as 21.9 ± 0.1 nm and 25.5 ± 0.1 nm for the Fe film and the Fe-Cu film, respectively. The grain sizes of the films are slightly affected by the variation of Cu content in the films. The preferential orientation of the films was found from relative peak intensities of the observed peaks in the XRD patterns using the relation indicated in Ref. [11]. While the crystal planes of Fe film are oriented in (100) direction, the (110) direction of bcc structure is predominant in the Fe-Cu film. It has been understood that the Cu content in the films affected the crystallographic structure of the films.

VSM measurements were performed to examine the relationship between the Cu content and magnetic

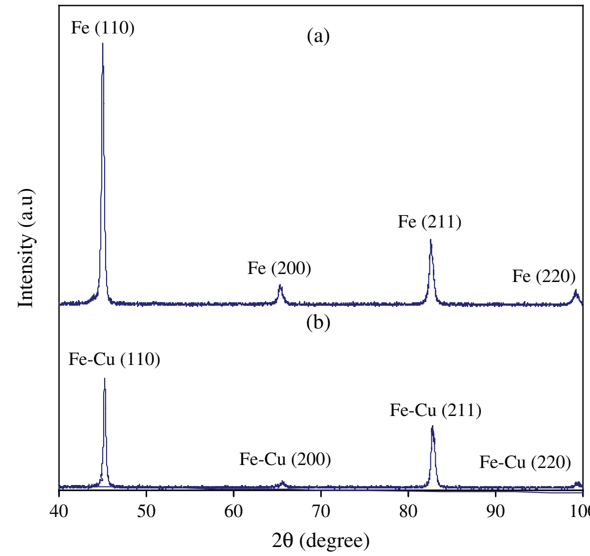

Fig. 3. XRD patterns of the films (a) The pure Fe film (b) The Fe-Cu film containing 9.5 wt% Cu and 90.5 wt% Fe.

properties of the films. Figure 4 shows the hysteresis loops of Fe-Cu films. In the in-plane hysteresis loops, the coercivity is 19.6 Oe, 23.1 Oe and 26.3 Oe, the saturation magnetization is 170.0 emu/cm^3, 141.6 emu/cm^3 and 122.7 emu /cm^3 for Fe film and Fe-Cu films containing 3.0 wt% Cu and 9.5 wt% Cu, respectively, see Table I. According to the results it was understood that the coercivity increases and the saturation magnetization decreases as the Cu content in the films increases. The films become magnetically harder due to the increase of non-magnetic Cu content in the films, as indicated in Ref. [12, 13]. To find the magnetization easy-axis, perpendicular hysteresis loops of the films were also measured. As an example to the perpendicular measurements, the hysteresis

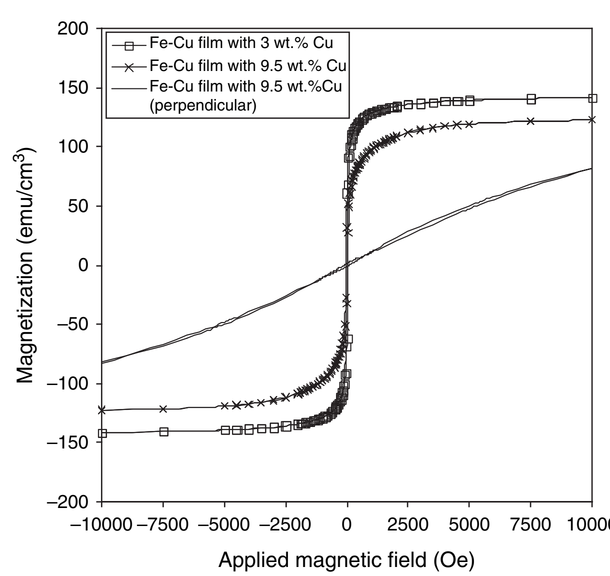

Fig. 4. The hysteresis loops of Fe-Cu films.

loop of the Fe-Cu film with 9.5 wt% Cu was presented in Figure 4. Since in-plane hysteresis loops have a higher remanent magnetization and lower coercivity than perpendicular loop, it was clearly understood that the easy-axis direction of the magnetization is parallel to the film plane.

4. CONCLUSIONS

The structural and magnetic properties of the Fe-Cu films were investigated as a function of Cu content in the films. In the results of the SEM images, it was seen that the Fe-Cu films with higher amount of Cu have cauliflower–like structure and rougher surface than Fe films. According to the microstructural analysis, the observed peaks belong to bcc phase of α-Fe due to the fact that low ratio of Cu (9.5 wt%) with respect to Fe films. However, the Cu content in the films affects the texture formation of the films because the (110) direction of bcc structure is predominant in the Fe-Cu film while Fe film has the orientation in (100) direction. In the magnetic point of view, VSM measurements showed that the higher amount of Cu content in films caused the harder magnetic properties. Furthermore, the easy-axis direction of the magnetization in the films is parallel to the film plane. Thus, it should be noted that the characteristics of electrodeposited Fe-Cu films can be changed by the Cu content in the films, and it is feasible to produce Fe-Cu films with desired properties, hence paving the way to produce magnetic films for sensor applications.

Acknowledgments: This work is supported by Balikesir University, Turkey under Grant no BAP 2005/18. The authors would like to thank Scientific and Technical Research Council of Turkey (TUBITAK) under Grant no TBAG–1771 for electrodeposition system and State Planning Organization, Turkey under Grant no 2005K120170 for VSM system. Thanks also go to the Anadolu University, Material Science and Engineering Department, Turkey and Dr. M.C. Baykul from Osmangazi University, Physics Department, Turkey for his help for EDX, SEM and XRD measurements.

References and Notes

1. P. C. Andricacos and N. Robertson, *IBM Journal of Research and Development* 42 **(1998)**.
2. M. Alper, Lecture Notes in Physics **(2002)**, Vol. 593, p. 111.
3. J. M. Williams, H. J. Blythe, and V. M. Fedosyuk, *J. Magn. Magn. Mater.* 155, 355 **(1996)**.
4. M. K. Roy and H. C. Verma, *J. Magn. Magn. Mater.* 270, 186 **(2004)**.
5. H. Topcu, M. S. Thesis, Balikesir University, Balikesir **(2003)**.
6. Y. Ueda and N. Kikuchi, *Jpn. J. Phys.* 32, 1779 **(1993)**.
7. E. Jartych, J. K. Zurawicz, E. Maczka, and J. Borc, *Materials Chemistry and Physics* 72, 356 **(2001)**.
8. W. C. Grande and J. B. Talbot, *J. Electrochem. Soc.* 140, 669 **(1993)**.
9. O. Karaagac, M. S. Thesis, Balikesir University, Balikesir **(2007)**.
10. B. D. Cullity, Elements of X-Ray Diffraction, Addison-Wesley, USA, **(1978)**, p. 105.
11. A. Vicenzo and P. L. Cavallotti, *Electrochem. Acta* 49, 4079 **(2004)**.
12. H. Kockar, M. Alper, and H. Topcu, *Eur. Phys. J.* 42, 497 **(2004)**.
13. D. Jiles, Introduction to Magnetism and Magnetic Materials, Chapman and Hall, London **(1991)**, p. 91.