Mater.Phys.Mech.1 (2000) 67-72

MECHANICAL AND MAGNETIC PROPERTIES OF POLYOL ELECTRODEPOSITED NiCo FILMS

G.M. Chow[1], Y.Y. Li[1] and Y.K. Hwu[2]

[1]Department of Materials Science, National University of Singapore Kent Ridge, Singapore 117543, Republic of Singapore
[2]Institute of Physics, Academia Sinica, Nankang, Taipei 11529, Taiwan, R.O.C.

Received: June 8, 2000

Abstract. The effects of applied voltage on the magnetic and mechanical properties of polyol electrodeposited NiCo films were studied and reported. Both electroless and electrolytic processes competed with each other during deposition. There existed a clear influence of voltage on the composition and magnetic properties of deposited films. However, a simple, systematic correlation of these properties with the structure, composition and microstructure could not be made. This lack of correlation was attributed to the complex variation of deposition chemistry with deposition time and voltage. It is conceivable that thick films deposited using long reaction time may have through-thickness inhomogeneity, thus obscuring the correlation of properties with the volume-averaged film characteristics.

1. INTRODUCTION

Nanostructured films may exhibit useful properties for many advanced applications because of the effects arising from size reduction and large amount of interfaces [I]. Recently we have used the polyol method to synthesize Cu film on A1N substrate [2] and Ni_xCo_{100-x} film on Cu substrate [3]. Polyol derived Ni-Co powders and films find various magnetic applications, for example, magnetoresistive sensors [4].

The polyol synthesis involves the reduction of metal precursors in ethylene glycol generally at the refluxing temperature of 194 °C. In this non-aqueous electroless process, the film deposition on substrate is accompanied by powder precipitation in solution. These two competing depositions may possibly affect the chemistry of the solution and the deposition chemistry at the fluid/solid interface, thus rendering the control of film properties difficult.

In powder precipitation the nucleation and growth of particles are controlled by the degree of supersaturation, which strongly depends on temperature. On the other hand, based on the relative standard potentials, the application of an electric field may selectively deposit metal films on the conductive substrate surface. The applied field may possibly minimize the free precipitation of metal powders in solution. Recently we have reported a study on the effects of reaction temperature and electric field on the polyol deposition of NiCo films [5]. It was found that compositional stoichiometry and microstructures were influenced by temperature, applied voltage and addition of sodium acetate (as a supporting electrolyte). The application of electric field promoted film deposition at low temperatures without concurrent powder precipitation. However, film deposition competed with powder precipitation at higher temperatures. At the refluxing temperature of 194 °C, the films were not stoichiometric as compared to nominal starting compositions. Further both electroless and electrolytic processes competed with each other at high temperatures.

In this paper we report the structural and magnetic properties of NiCo films synthesized using 1 h deposition lime at 194 °C under different applied voltages. The starting precursor composition of Ni:Co was kept at 50:50. The relationships of properties and processing parameter were discussed.

2. EXPERIMENTAL

Nickel (II) acetate tetrahydrate and cobalt (II) acetate tetrahydrate were dehydrated at 120 °C in an oven for 5 h prior to experiments. 0.05 M nickel acetate and 0.05 M cobalt acetate were suspended in 200 ml of ethylene glycol, to give a nominal film composition of $Ni_{50}Co_{50}$. 0.5 M dehydrated sodium acetate (NaAc) was also added to improve the electrical conductivity of the reaction mixture.

Corresponding author: G.M. Chow, e-mail: mascgm@nus.edu.sg

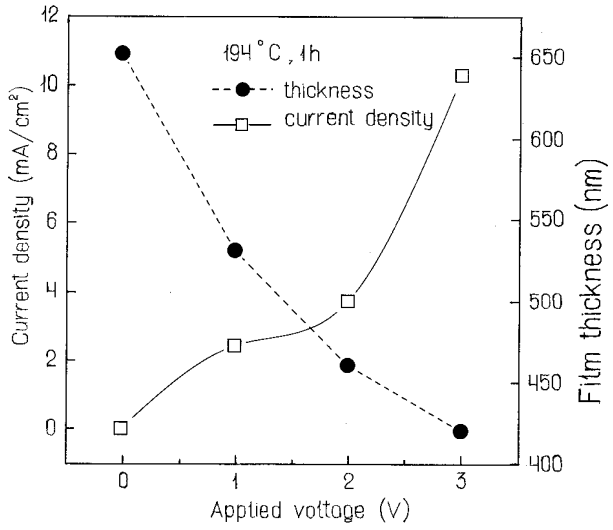

Fig. 1. Dependence of current density and film thickness on deposition voltage.

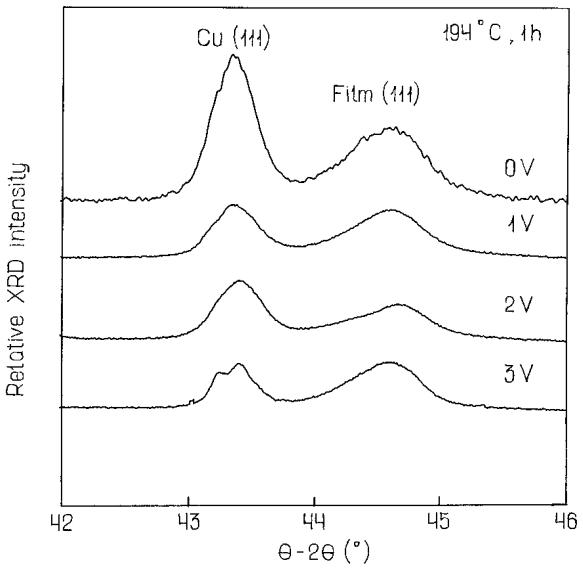

Fig. 2. XRD of films deposited at different voltages.

Polished polycrystalline Cu substrates with a (200) bulk texture were vertically suspended in the mixtures as cathodes. The substrate was connected to a copper wire as a typical electrochemical specimen and was degreased with acetone and washed thoroughly before use. The anodes were platinum lattice grids of similar size as the Cu substrates. A constant potential of 0 V, 1.0 V, 2.0 V or 3.0 V was applied during electrodeposition at the refluxing temperature of 194 °C. Deposition time was kept for 1 h after the mixture reached the reaction temperature in question. The current density decreased initially and became constant within 10 min. After deposition the films were air-dried and rinsed with acetone. The long-range order of the films was studied using X-ray diffraction (XRD) at a glancing incidence of 1°. The crystallite size was estimated from XRD line broadening. The microstructure was studied using scanning electron microscopy (SEM) and the composition was confirmed using SEM energy dispersive X-ray (EDX) analysis. The thickness of cross-sectioned films was measured using SEM imaging and EDX mapping. The local atomic environment of the films was investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy at the beamline 3C1, Pohang Light Source, S-Korea. The magnetic hysteresis loops were measured using vibrating sample magnetometry (VSM) in the parallel (//) and perpendicular (⊥) directions to the film plane using a maximum magnetic field of ±50kOe. The Vickers microhardness (HV) of Ni-Co films on Cu substrates was measured using a load of 10 gf for 10 s. Microscratch tests for film adhesion were performed to determine the critical load of delamination, A diamond tip (50 μm radius) with a load from 0 to 3 N was used, with a loading rate of 1.5 N/min and a scratch speed of 1.5 cm/min.

3. RESULTS AND DISCUSSIONS

The dependence of current density and film thickness on applied voltage is shown in Fig. 1. The current density increased whereas the film thickness decreased with increasing voltage. The decrease of film thickness with increasing current density was explained by the formation of hydrogen as a result of solvent breakdown [5]. Hydrogen bubbles physically pushed the electrolyte away from the deposition zone, possibly stopping the electroless and hindering the electrolytic processes. Glancing angle XRD showed the films were polycrystalline. Fig. 2 shows the (111) peaks of the Cu substrates and deposited films. There was no noticeable difference among the films deposited at different voltages. Nickel and Co have mutual miscibility and are expected to form solid solutions. The XRD results showed no elemental peak separation and a set of single peaks suggested the formation of solid solutions. However, using anomalous x-ray scattering we recently have shown that nanostructured NiCo films did not necessarily form a solid solution as expected from their phase diagram or suggested by the results of conventional XRD [6]. Therefore, we could not ascertain if the films in this work were alloys or composites using only the conventional XRD data. Fig. 3 shows the relationships of Co concentration and crystallite size (estimated from (111) line broadening) with voltage. The film composition deviated from the starting nominal compositions of 50:50, and Ni concentration was significantly higher for films deposited at high

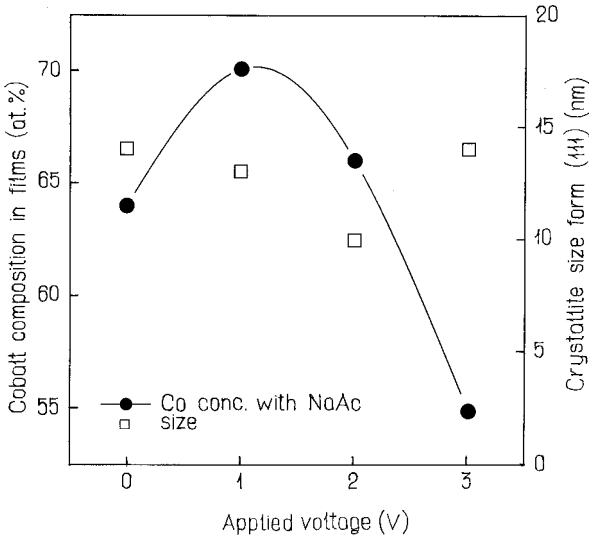

Fig. 3. Dependence of Co concentration and film's (111) crystallite size on voltage.

voltage. The crystallite size, however, showed no dependence on concentration and voltage.

The microstructures of deposited films as a function of applied voltage are shown in Fig. 4. It can be seen that films deposited at low or no voltage had higher apparent density (Figs. 4a and 4b). Deposition at 2 V (Fig. 4c) resulted in larger particles whereas at 3V porous film with elongated particles (Fig. 4d). Note that the particles shown in SEM consisted of nanostructured crystallites with size estimated from the XRD coherence length as discussed before.

The hysteresis loops of deposited films showed magnetic saturation. Fig. 5 shows the dependence of saturation magnetization (M_s) with Co concentration and voltage. The M_s of bulk fcc Ni, fcc Co and hcp Co are 484, 1538 and 1442 emu/cm^3, respectively. The M_s followed the Co concentration for films deposited in the range of 0 - 2 V. For the film deposited at 3 V (with a composition of $Ni_{45}Co_{55}$), the M_s reached 1034 emu/cm^3 despite a lower Co concentration and higher film porosity (see Fig. 4c). A much higher M_s should be expected if the film had been denser. However, the M_s of this porous film with similar composition compared well with the bulk $Ni_{50}Co_{50}$ (997 emu/cm^3) [7] and the electroless polyol-derived $Ni_{50}Co_{50}$ film (1016 emu/cm^3) [3]. The films deposited at 0 and 2 V had a higher perpendicular coercivity compared to their respective parallel coercivity. For example, the films deposited at 0 V had a perpendicular coercivity of 460 Oe, which was almost 4 times higher than that in the parallel direction. The results on coercivity, which depends on complex relationships of particle size, microstructure and grain boundary chemistry, did not show any clear dependence on composition and microstructure (Fig. 6).

The long-range order of deposited films was quite similar as shown in the XRD results above. The local atomic environment of Ni in these films deposited at

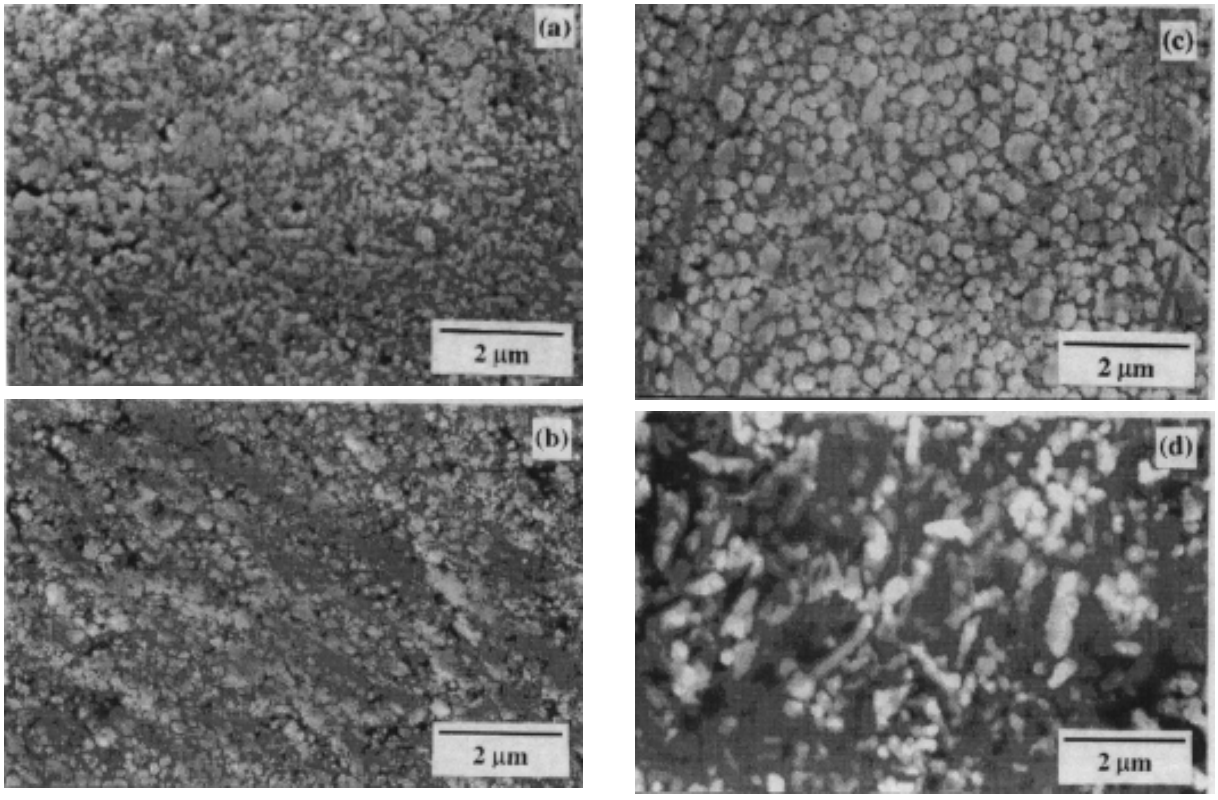

Fig. 4. SEM micrographs of NiCo films deposited at 1 h: (a) 0V, (b) 1 V, (c) 2 V, and (d) 3V.

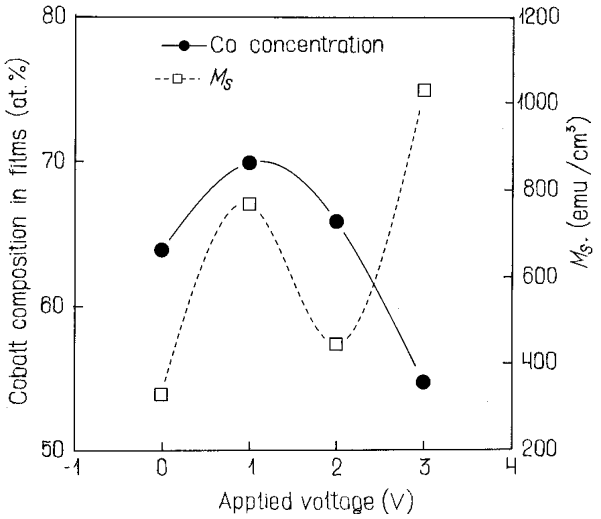

Fig.5. Relationships of Co concentration and saturation magnetization.

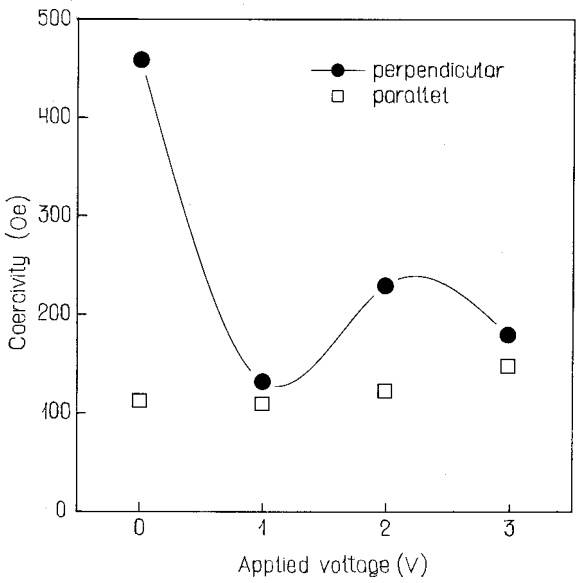

Fig. 6. Dependence of coercivity on voltage.

different voltages was also very similar, as shown in Fig. 7a. However, the local atomic environment of Co became more disordered with increasing voltage (Fig. 7b). The coordination of the first shell of Co decreased from 9.4 to 6.7 with increasing voltage. However, there seemed to be no direct relationships between the local atomic environment and the magnetic properties.

Fig. 8 shows the relationships of microhardness and adhesion properties of deposited films. The Vickers hardness (HV) was in the range of 100 - 110, and the critical load for film delamination was around 1.9 N. The deposited films, despite the difference in composition and Co local atomic environment, showed similar mechanical properties.

It is clear that the application of electric field influenced the composition, local atomic environment of Co and the microstructure of these films. Yet, the lack of apparent correlation of magnetic properties with composition and the local atomic environment of Co needs to be addressed. Saturation magnetization depends on the factors such as composition and crystallinity, and coercivity on composition, microstructure and particle size. The probing techniques used in this work, such as XRD, EXAFS, EDX and VSM, provide only the volume-averaged information in the samples. Such averaged information can be well used to characterize the sample, based on the assumption that the sample is homogeneous. We further

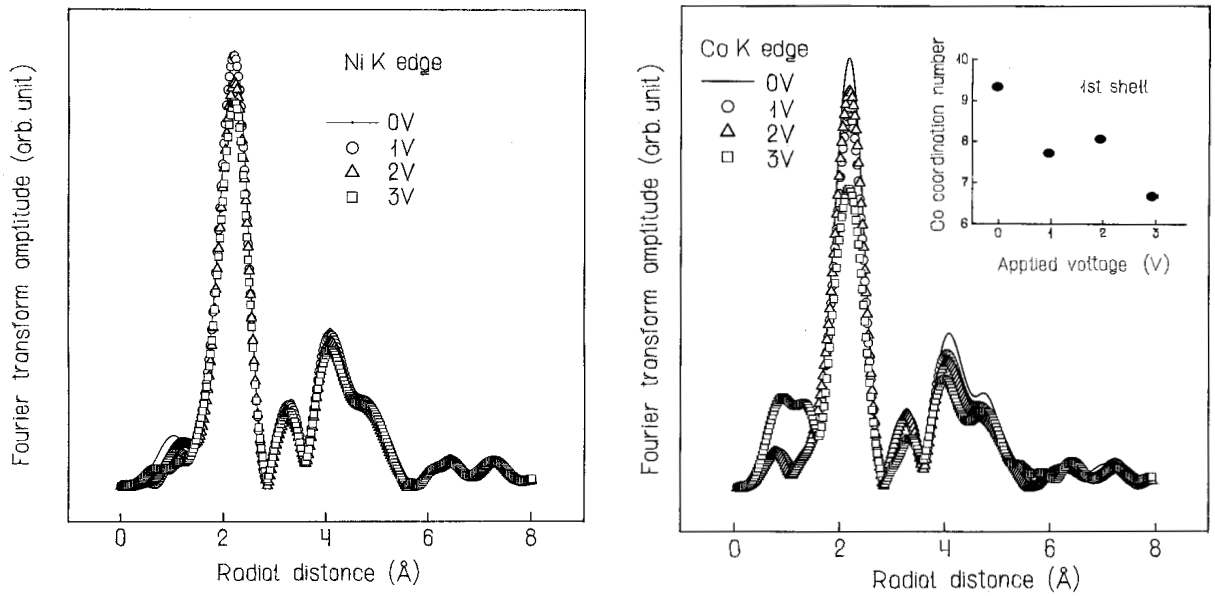

Fig. 7. EXAFS results of local atomic environment of deposited films, (a) Ni K-edge, (b) Co-K edge, inset shows the Co coordination number as a function of applied voltage.

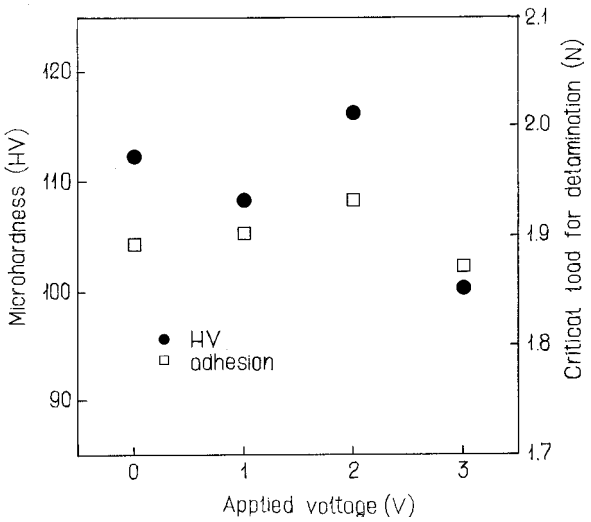

Fig. 8. Dependence of microhardness and critical load for delamination on voltage.

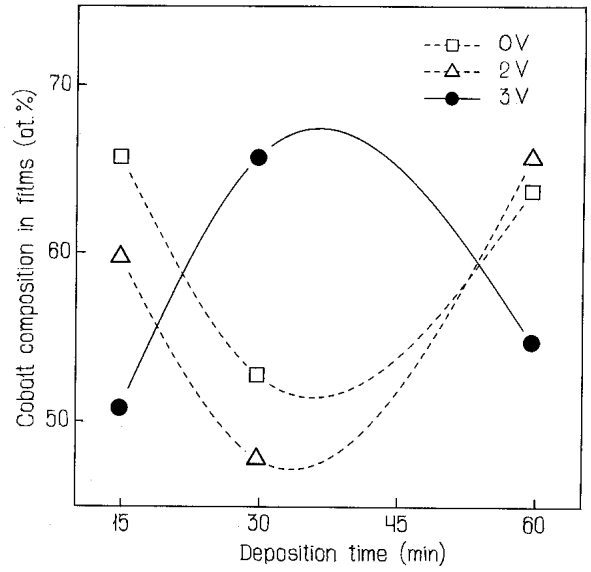

Fig. 9. Relationships of Co composition with deposition time and voltage.

investigated the homogeneity of films deposited at 1 h by studying the films deposited under the same conditions using different deposition times. If the deposition chemistry did not vary within a given time frame, the films deposited under the same conditions at different times generally possess similar characteristics and properties. If the solution chemistry changed with increasing time, there would exist through-thickness inhomogeneity (in terms of composition, structure and microstructure) in films deposited at longer time. Since the deposition temperature was well below half the melting temperatures of Ni and Co, the diffusion process to achieve through-thickness homogeneity was not expected to occur. Fig. 9 and 10 indeed showed the variation of composition and M_s with increasing deposition time, respectively. These findings strongly suggest that there existed through-thickness inhomogeneity in the polyol-electrodeposited films, particularly for those deposited at long reaction time. Similar composition dependence on deposition time has also been recently reported in electroless polyol-deposited NiCo films [8]. In this current work, the application of electric field further complicated the solution chemistry, as both electroless and electrolytic depositions competed with each other. It seems that the magnetic properties were more sensitive to the inhomogeneities than the mechanical properties, as the length scale of through-thickness inhomogeneities may not be significant under the current mechanical measurement conditions. More work, such as transmission electron microscopy and spectroscopy techniques, are currently underway to investigate the through-thickness microstructures and chemistry.

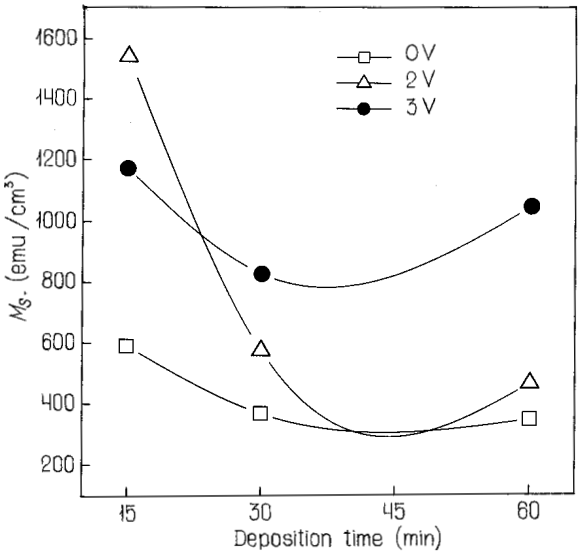

Fig. 10. Relationships of M_s with deposition time and voltage.

4. SUMMARY

The effects of applied voltage on the properties of polyol electrodeposited NiCo films were studied. Both electroless and electrolytic processes competed with each other during deposition. There existed a clear influence of voltage on the composition and magnetic properties of deposited films. However, a simple, systematic correlation of these properties with the structure, composition and microstructure could not be made. This lack of correlation was attributed to the complex variation of deposition chemistry with increasing deposition time and voltage. It is conceivable that thick films deposited using long reaction time may have through-thickness inhomogeneity, thus obscuring the correlation of properties with the volume-averaged film characteristics.

ACKNOWLODGMENTS

G.M.Chow thanks the support of this work by the National University of Singapore and the US Office of Naval Research. Y.Y. Li was supported by the NUS postgraduate research scholarship.

REFERENCES

[1] *Nanostructured Films and Coatings, NATO Science Series, 3, High Technology*, ed. by G.M. Chow, I. Ovid'ko and T. Tsakalakos **78** (Kluwer Academic Publishers, Dordrecht, 2000).

[2] G.M, Chow, L. K. Kurihara, D. Ma, C. R. Feng, P.E. Schoen and L.J. Martinez-Miranda // *Appl. Phys. Lett.* **70** (1997) 2315.

[3] G.M. Chow, J. Ding, J. Zhang, K.Y. Lee, D. Surani and S.H. Lawrence // *Appl. Phys. Lett.* **74**(1999)1889.

[4] A. Bianco, G. Gusmano, G. Montesperelli, B. Morten, M. Prudenziati, R. Zanoni and G. Righini // *Thin Solid Films* **359** (2000) 21.

[5] Y.Y. Li, W.C. Goh, D.J. Blackwood, Y.Z. Huang and G.M. Chow, in preparetion.

[6] G.M. Chow, W.C. Goh, Y.K. Hwu, T.S. Cho, J.H. Je, H.H. Lee, H.C. Kang, D.Y. Noh, C. K. Lin and W. D. Chang // *Appl. Phys. Lett.* **75** (1999) 2503.

[7] C. Sadron // *Ann. Phys. Paris*. **17** (1942) 371.

[8] J. Zhang and G.M. Chow // *J. Appl. Phys.*, in press.