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NANOSTRUCTURED Ni FILMS BY POLYOL ELECTROLESS DEPOSITION

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Abstract. Nanostructured Ni films were deposited on Cu by reducing nickel acetate tetrahydrate in refluxing ethylene glycol at about 194 °C. The effects of deposition time (t) and Pt as nucleating aid were investigated in this polyol process. The solution chemistry varied with t. At longer t, corrosive attack of the solvent on deposited films led to dissolution and re-deposition of Ni. Saturation magnetization increased with t and decreased with increasing Pt precursors. The deposited Ni films were magnetically saturated. They showed in-plane magnetization anisotropy and perpendicular coercivity anisotropy. The use of Pt caused rapid powder precipitation but did not enhance film deposition. The Pt-catalyzed Ni films showed a (200) texture and a higher squareness ratio.

1. INTRODUCTION

Nanostructured films have attracted much attention because of their unique properties that arise from effects of size reduction and large amount of interfaces [1]. These films can be prepared by many methods, for example, sputtering, laser ablation, electrodeposition and electroless deposition. For uniform metallization of non-planar and/or hidden surfaces, solution chemistry is better suited than the physical vapor methods, since it is not limited by the line-of-sight deposition.

An electroless polyol method, which has been mainly used to synthesize micron, submicron and nanostructured powders [1-8], has been recently applied for deposition of nanostructured metal films, for example, Cu film on AlN substrate [9] and Ni_xCo_{100-x} film on Cu substrate [10]. The Ni_xCo_{100-x} films exhibited good magnetic properties with perpendicular coercivity anisotropy [10]. The structure of these films have been recently investigated using anomalous x-ray scattering to determine if a solid solution or phase-separated composite was formed and the element-selected long range order [11]. To date, the film deposition chemistry and mechanisms of this polyol process are not yet well understood. Unlike physical vapor deposition where the flux of atoms can be maintained constant, the solution chemistry (thus deposition chemistry) may vary as a function of deposition (reaction) time.

In this paper, we report our investigation of the magnetic properties of polyol-deposited Ni films and their dependence on the deposition time (t). The effects of increasing t on crystallite size, film thickness, microstructures and magnetic properties were studied. The influence of Pt as nucleating aid, which has been used in polyol synthesis of powders [12], on Ni film deposition was also studied.

2. EXPERIMENTAL

Polycrystalline, coarse-grained copper with (200) texture was used as substrates without any pre-deposition surface treatment or polishing. 0.1 M nickel acetate tetrahydrate was suspended in 200 ml ethylene glycol. Hexachloroplatinic acid in small quantity was added in reactions where the effects of nucleating aid were investigated. The ratio of concentration of Pt to Ni ([Pt]/[Ni]) was estimated from the starting precursors. The substrate was vertically suspended in the mixture, which was brought to reflux at about 194 °C. Deposition time (t = 0.5, 1, 2 and 3 h) was taken on the base of the time required to reach the the refluxing temperature. After each deposition, the coated sample was immediately removed from the mixture, rinsed with

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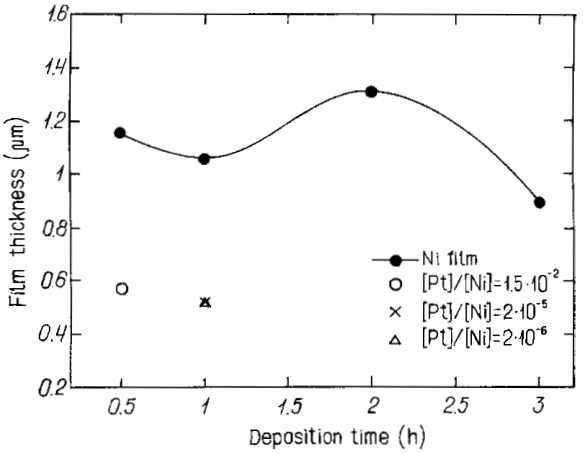

Fig. 1. Dependence of Ni film thickness on deposition time.

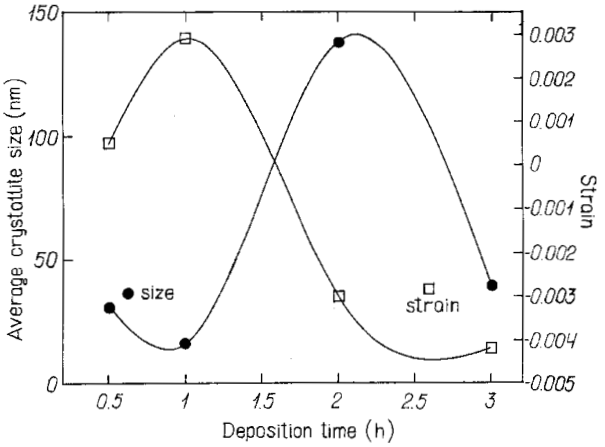

Fig. 2. Dependence of crystallite size and strain on deposition time.

distilled water and acetone or 2-propanol, and subsequently air-dried for characterization.

The structure of the films was studied using x-ray diffraction (XRD) in the θ-2θ mode. The diffraction peaks were analyzed using a profile fit routine and the FWHM of the specular peaks were used for estimation of average crystallite size and strain of these films. It was assumed that the total line broadening (B_{total}) was the linear sum of that due to size and strain. A plot of ($B_{total}\cos\theta$) *vs* $\sin\theta$ yielded the strain and the size from the slope and intercept, respectively. The microstructure was investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Cross-sectioned samples were checked with SEM for film thickness determination. The hysteresis loops were measured using vibrating sample magnetometry (VSM) in the parallel (//) and perpendicular ($\perp$) directions to the film plane using a maximum magnetic field of ± 50kOe.

3. RESULTS AND DISCUSSIONS

The dependence of film thickness on t and the [Pt]/[Ni] is shown in Fig.1. For t = 3 h, the decrease in film thickness may be related to the corrosive attack of ethylene glycol on deposited Ni films. It has been reported for other systems involving chemical oxidation of ethylene glycol at elevated temperatures, oxalic acid was identified as a product. Both it and various organic acids that were formed as intermediates are corrosive to metals [13]. Nickel and Pt are miscible below 200 °C. When Pt was used as nucleating aid, the reaction completed at about 0.5 h for [Pt]/[Ni] of $1.5\cdot10^{-2}$. When [Pt]/[Ni] $\leq 2\cdot10^{-5}$, the reaction took about 1 h to finish. The use of Pt precursors for aiding nucleation of Ni nanocrystals has been reported [12]. The similar results were reported for Pd(II) and Cu(II) acetates in 2-ethoxyethanol at 135 °C, in which initial Pd reduction assisted the reduction of copper [14]. In this work, Pt precursor only promoted rapid precipitation of Ni powder but it did not enhance film deposition, since thinner films were obtained compared to those deposited without Pt (Fig. 1). The undesirable competition between powder precipitation and film formation can be minimized by application of electric field during deposition and lower deposition temperature [15].

The XRD results showed that Ni was polycrystalline fcc. The average crystallite size and strain of Ni films are shown in Fig. 2. The crystallite size reached a maximum of about 138 nm at t = 2 h, but it significantly decreased to 40 nm at t = 3h. The decrease in crystallite size and film thickness at longer t was the result of corrosive attack of the solvent on the deposited films, leading to dissolution and re-deposition of finer particles. The micro-strain of these films changed from tensile to compressive with increasing t. Fig. 3 shows the SEM micrographs of Ni films deposited at t = 2 and 3 h, respectively. It can be seen that sintering of films occurred (thus largest crystallite size as shown in Fig. 2) at t = 2 h, whereas finer particles were observed in film deposited at t = 3 h. Note that the particles seen in SEM consisted of nanostructured crystallites (measured by x-ray line broadening). Fig. 4 shows a TEM micrograph of Ni crystallites on Cu substrate deposited at t = 2h.

The XRD patterns of Ni films prepared using Pt catalysts only showed only Ni, without any evidence of Pt as a separate phase. The average crystallite size (estimated from (111) line broadening) increased with decreasing [Pt]/[Ni] precursor molar ratio from 33 to about 70 nm. The similar results of dependence of Ni particle size on Pt nucleating aid was reported in the polyol synthesis of Ni powders [12].

The Ni films were magnetically saturated. Both Ni and Pt-catalyzed Ni films exhibited in-plane magnetization anisotropy. Fig. 5 shows the $M_{s//}$ and $M_{s\perp}$ for Ni films deposited at 0.5 and 3 h. Fig. 6 shows the depen-

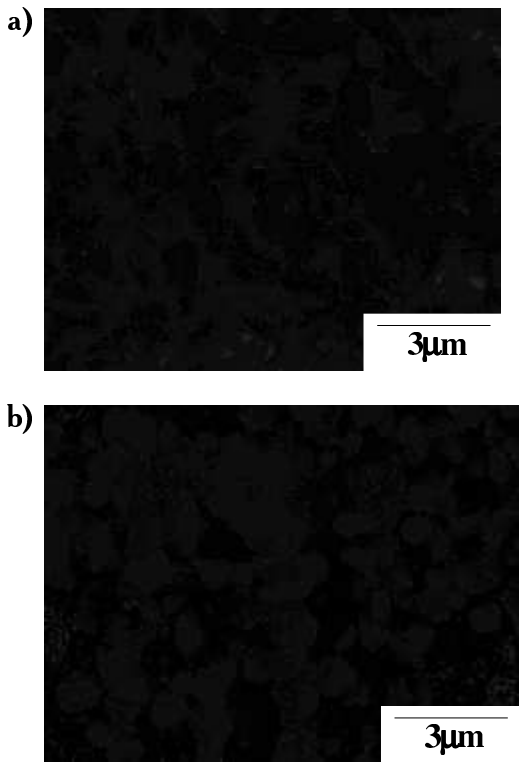

Fig. 3. SEM micrographs of Ni films deposited at : **a)** 2 h, **b)** 3 h.

Fig. 4. TEM bright field micrograph of Ni film on Cu substrate deposited at 2 h. Dark particles are Ni.

dence of $M_{s//}$, $H_{c//}$ and $H_{c\perp}$ of Ni films on t. The M_s of bulk fcc Ni is about M_s is 484 emu/cm^3. The values of $M_{s//}$ increased with t and reached 405 emu/cm^3 for the Ni film deposited 3 h. This may be due to the increased film density at longer t. For films consisting of randomly oriented crystallites, the squareness ratio (ratio of remanent magnetization, M_r, to saturation magnetization, M_s) is typically about 0.5. This ratio was between 0.4 and 0.5 for Ni films, except it was higher for that deposited at 1 h (about 0.6). Fig. 7 shows $M_{s//}$ and the squareness ratio of Ni films deposited with Pt catalysts. $M_{s//}$ increased whereas squareness ratio

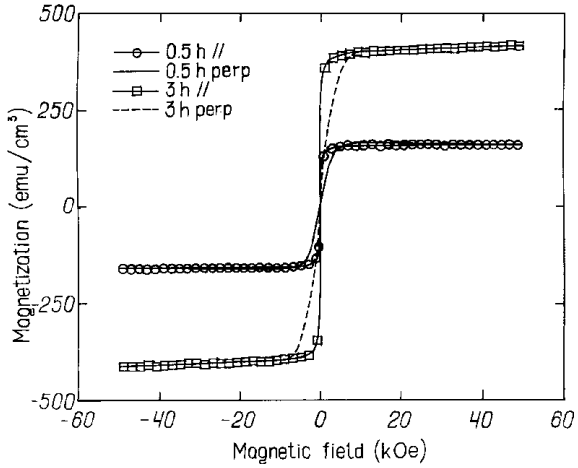

Fig. 5. Hysteresis loops of Ni films deposited at 0.5 h and 3 h, showing magnetic saturation and in-plane anisotropy.

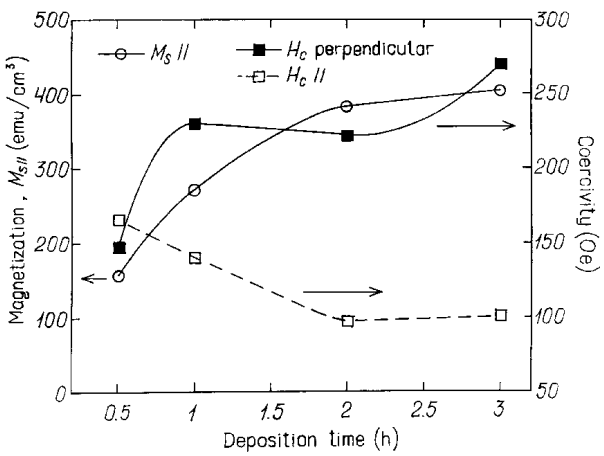

Fig. 6. Dependence of saturation magnetization and coercivity of Ni films on deposition time.

decreased with decreasing [Pt]/[Ni]. The deposition time for Ni films using [Pt]/[Ni] of $2{\cdot}10^{-5}$ and $2{\cdot}10^{-6}$ was about 1 h, and was 0.5 h for [Pt]/[Ni] of $1.5{\cdot}10^{-2}$. Pt had a predominant effect on $M_{s//}$ and a lower [Pt]/[Ni] ratio led to a higher M_s as expected. Lower M_s may be related to alloying of Pt with Ni. Examination of XRD data of these films showed a (200) texture. This is consistent with the higher squareness ratio (between 0.56 to 0.65) of these films. Fig. 8 shows that the films deposited with Pt catalysts also had higher perpendicular coercivity. The coercivity anisotropy may be related to the microstructures of deposited film [15]. The work is currently underway to investigate the structure and microstructure of these films by transmission electron microscopy.

4. SUMMARY

Nanostructured Ni films were deposited by the polyol method on Cu substrates with or without Pt as nucleating aid. The solution chemistry varied with t. At longer

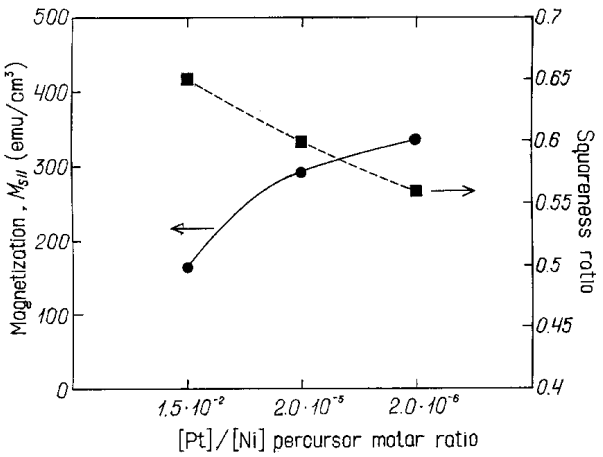

Fig. 7. Dependence of saturation magnetization and square ratio of Ni films on [Pt]/[Ni] precursor molar ratio.

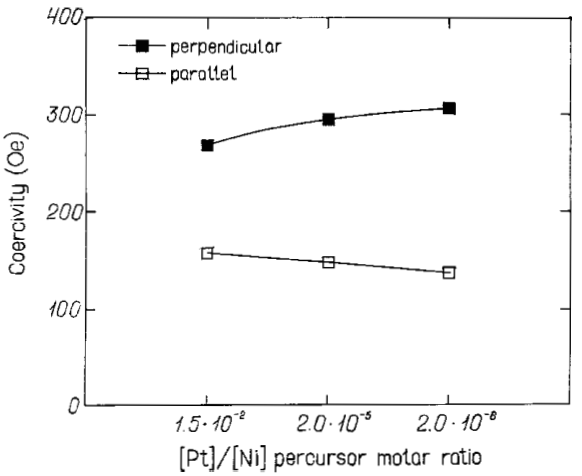

Fig. 8. Dependence of coercivity of Ni films on [Pt]/[Ni] precursor molar ratio.

t, corrosive attack of the solvent on deposited films led to dissolution and re-deposition of Ni. Saturation magnetization increased with *t* and decreased with increasing Pt precursor concentration. The magnetically saturated films showed in-plane magnetization anisotropy and perpendicular coercivity anisotropy. The use of Pt favored rapid powder precipitation but did not enhance film deposition. The Pt-catalyzed Ni films showed a (200) texture and a higher squareness ratio. Further work is needed to understand the solution chemistry and film deposition chemistry in the polyol process.

ACKNOWLEDGMENTS

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