

# NANOSTRUCTURED IRON-NICKEL THIN FILMS SYNTHESIZED BY ELECTROLESS POLYOL DEPOSITION

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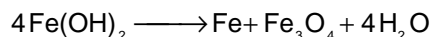
**Abstract.** Fe<sub>x</sub>Ni<sub>100-x</sub> thin films were deposited on conductive (Cu) and non-conductive (Pd activated glass) substrate using an electroless, polyol method. The stoichiometry of film composition, as compared to the precursor concentration, strongly depended on the substrate position. When the substrate was immersed in the refluxing solution, Fe-deficient films were deposited. However Fe-rich films were synthesized when the substrates were suspended in the vapor phase above the solution. When the substrate was repeatedly suspended above the solution for a short time after each long immersion in solution (this process was denoted as quenching), the films developed an intermediate range of Fe concentration. The surface microstructure, long range and short range orders of these films revealed that the films were oxidized, and the extent of oxidation depended both on the type of substrate and substrate position.

## 1. INTRODUCTION

Iron-nickel thin films find uses in magnetic recording heads due to their low coercivity, high permeability and near zero magnetostriction [1]. Solution synthesis of FeNi thin film using conventional electrodeposition has been reported [2-6]. Electroless deposition depends on the auto-catalytic chemical reaction without any applied current. However, it requires the initial functionalization of the substrate. The most attractive advantage of electroless deposition over electrodeposition is that it is suitable for a large range of substrates, which can be conductive or non-conductive and with regular or irregular surface.

A non-aqueous electroless process known as the polyol method has been used to produce fine powders. It involves reduction of metal precursors in refluxing ethylene glycol (EG). Noble metals such as silver [7], palladium [8], copper [9] and even less easily reducible metals such as nickel [10] and nickel-cobalt alloy [11] can be prepared by precipitation in the alcohol media. The polyol process however is not suitable for the synthesis of Fe. Since Fe has a more negative standard reduction poten-

tial in EG than Ni [ $E_{298}^0(\text{Fe}^{2+}/\text{Fe}) = -1.240 \text{ V}$ ,  $E_{298}^0(\text{Ni}^{2+}/\text{Ni}) = -0.926 \text{ V}$  with respect to AgCl/Ag reference electrode] [12], EG is too weak to reduce Fe<sup>2+</sup>. The disproportionation of Fe(II) hydroxide has been reported in Fe-Ni codeposition according to the following reaction [13,14].

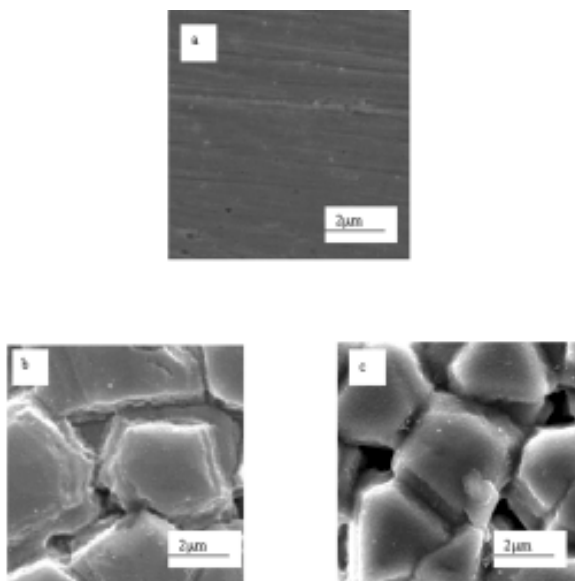


To increase the yield of Fe, a large excess of sodium hydroxide with respect to iron (II) is necessary. In such FeNi codeposition, polyols play several important roles as: (1) solvent and reaction media; (2) reducing agent for Ni precursor; (3) protecting agent to prevent oxidation in both Ni and Fe deposition; and (4) complexing agent to prevent the crystallization of magnetite (Fe<sub>3</sub>O<sub>4</sub>) in Fe deposition. However, due to the low yield of Fe disproportionation, Fe concentration in synthesized FeNi particles was still below 30 at.%, and could not be increased even by enhancing the ratio of Fe precursor [14]. To date, little work has been reported on the polyol deposition of FeNi thin film.

In this paper, we report our study of the polyol deposition of FeNi films using both conductive substrate (polycrystalline Cu) and non-conductive sub-

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**Fig. 1.** SEM micrographs of Cu and etched glass substrates (a) Cu substrate; (b) 25 nm Pd film sputtered on etched glass; (c) 2 nm Au film sputtered on etched glass.

strate (etched glass). During film deposition black Fe-rich deposits were observed on the glassware above the solution surface. This phenomenon suggested that in the polyol system, the Fe deposition was not confined only in the solution phase, but it also occurred in the vapor phase. Moreover, Fe deposition might be favored in vapor instead of in the solution. To gain further insight into this process, the effects of varying the substrate position was investigated. Three deposition processes were studied: a) the substrate was completely immersed in solution; b) the substrate was repeatedly immersed in solution followed by a brief suspension above the solution (referred to as quenching); and c) the substrate was completely suspended in the vapor above the solution.

## 2. EXPERIMENTAL METHODS

Two solutions were mixed: the first being a mixture of the metal salts, nickel (II) acetate tetrahydrate and iron (II) acetate in the molar ratio of 50:50, in a total concentration of 0.2 mol/l after mixing; and the second solution contained sodium hydroxide in excess with respect to the metal salt stoichiometry, i.e. sodium hydroxide concentrations in the range 2.0 mol/l after mixing. Different substrates (polished Cu and etched glass) were vertically suspended and used in three different deposition processes, namely, in solution, above solution and quenching. Quench-

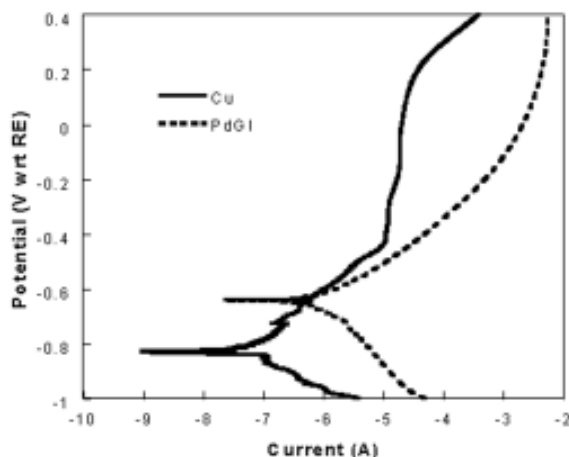
ing was carried out such that during every 10 min deposition, the substrate was kept in the solution for 7 min and above the solution for 3 min.

The solution was heated to the refluxing temperature of 194 °C and refluxing was allowed to continue for 60 min. During heating, nitrogen was introduced to the reaction solution to prevent metal ions from oxidation. The composition of the deposited films was determined by energy-dispersive X-ray spectroscopy (EDX). The surface morphology of the films was observed using scanning electron microscopy (SEM). The long-range order of the films was studied using  $\theta$ -2 $\theta$  X-ray diffraction (XRD) and the peaks were analyzed using a profile fit routine. The average crystallite size was estimated from the line broadening at the full width half maximum, ignoring the strain broadening. The local atomic environment of the films was investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy at beamline 3C1, Pohang Light Source, South Korea.

## 3. RESULTS AND DISCUSSION

**Characterization of Substrates.** The surface of polished Cu substrate was fairly smooth with some fine scratches as shown in Fig. 1(a). The deposition of FeNi films occurred on Cu substrate irrespective of the substrate position. However, film deposition was not observed for etched glass substrates. This indicated that the nature of the substrate played a very important role in electroless deposition. Accordingly, it was necessary to activate the non-active glass substrate by introducing catalytic particles prior to electroless deposition. Palladium is frequently used as an activator for electroless plating of many metals and alloys [15]. In our work, glass substrates were activated with a sputtered Pd film. The thickness of the Pd interface was about 25 nm. Faceted structures were found in the SEM micrograph as shown in Fig. 1(b). To investigate whether the facets were from the etched glass or the crystalline layer of the Pd interface, a Au film with a thickness of 2 nm was sputtered on the etched glass substrate and its morphology was shown in Fig. 1(c). There was no noticeable difference between the thin Au and thicker Pd interface. It could be concluded that the etched glass itself was faceted, and they were covered by the thin metal interface after sputtering. For discussion, the etched glass substrate with Pd interface is denoted as PdGI.

The catalytic activities of different substrates were evaluated from the anodic polarization curves in EG (Fig. 2). It was found that the apparent oxidation potential of EG on Cu was lower than that on PdGI.



**Fig. 2.** Polarization curves for the anodic oxidation of ethylene glycol solution containing 2 mol/l NaOH on different substrates.

Thus Cu substrate was more active than PdGI in the alkaline EG solution. Although Pd was very effective to activate substrate in many reductant systems, such as borohydrides, hydrazines and hypophosphites, it was not a universally active catalyst for all anodic oxidation of reductant. Furthermore the large Pd faceted particles (>2  $\mu\text{m}$ ) may not be as active as that of nanometer colloidal Pd catalysts.

**Film Composition.** The composition of FeNi films deposited on Cu and PdGI substrates suspended at different positions is shown in Table 1. As mentioned before, FeNi film could be deposited on Cu substrate in three different positions, but the film composition greatly differed. For the PdGI substrate, film deposition occurred only when the substrate was quenched or suspended above the solution. When the substrate was immersed in the solution, Pd interface was not adhesive enough to survive the refluxing reaction system and finally peeled off. Further adhesion measurement showed that the critical load for the delamination of Pd interface was 2.92 N (determined by micro-scratch test using a progressive load from 0 to 5 N at a loading rate of 2.5 N/min).

When the Cu substrate was immersed in solution, Fe concentration of deposited films was 25%. The Fe deficiency has been explained by the low yield of Fe disproportionation that resulted from the unavoidable oxidation of  $\text{Fe}(\text{OH})_2$  and Fe particles [14]. Changing the substrate position however dramatically influenced  $x$  for both substrates. The Fe concentration increased when the substrate was

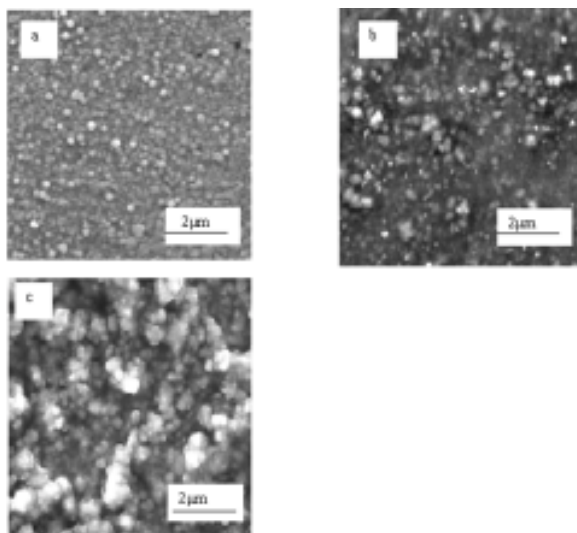
**Table 1.** Fe concentrations of FeNi films deposited on different substrates.

Substrate	Substrate position	$x$ in $\text{Fe}_x\text{Ni}_{100-x}$ ( $x$ in at.%)	Film thickness (nm)
Cu	In solution	25	322
	Quenching	41	298
	Above solution	90	285
PdGI	In solution	No film	Not available
	Quenching	63	462
	Above solution	87	407

suspended above the refluxing solution. When the substrate was quenched, the films developed an intermediate range of  $x$ . Similar film compositions were obtained using a different starting ratio of Fe of 70% (data not shown here) and the similar dependence of Fe concentration on substrate position was also confirmed on both Cu and PdGI substrates. When the substrate was placed in or above the solution, solution deposition or vapor deposition occurred on the substrate surface, respectively. When the substrate was quenched, it experienced the two deposition mechanisms repeatedly. Vapor and solution deposition might have different mechanisms of nucleation and growth due to presumably different transport mechanisms of atoms and interfacial reactions. Enhancement of Fe concentration in the FeNi films deposited in the vapor phase of the polyol process has been suggested resulting from the formation of Fe-Ni-EG intermediates [16].

It was noted that for quenching-deposited films, the Fe concentration on PdGI substrate was much higher than that on Cu substrate. The reason is not yet clear, but it may be related to the interfacial reactions of Pd in the reduction or disproportionation occurred in solution.

**Morphology.** Fig. 3 shows the surface morphology of deposited thin films on Cu substrates. All of the three samples had high apparent film density. However, the vapor phase deposition seemed to show rougher surface as compared to the other processes. The apparent particle size increased from solution deposition to vapor deposition. The film deposited in vapor had the largest apparent particle size (in SEM) and smallest crystallite size (about 50 nm, estimated from X-ray coherence length). This indicated that the small crystallites agglomerated to form large particles without significant grain

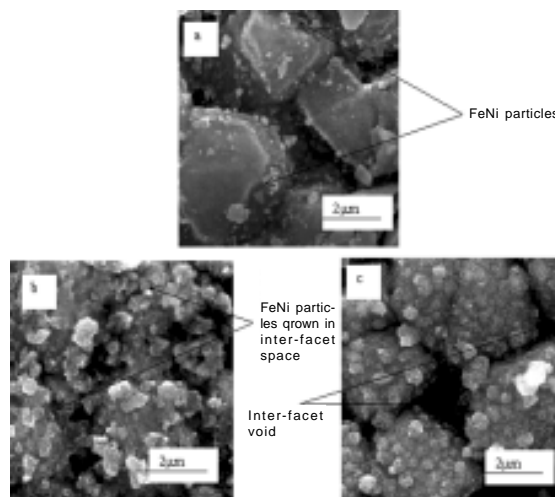


**Fig. 3.** SEM micrographs of FeNi thin film (a) in solution, (b) quenched, (c) above solution.

growth. The charging effect (bright spots in SEM) could be attributed to the existence of oxide. A comparison of the three SEM micrographs showed that vapor-deposited film had more surface oxide than solution-deposited film.

In this work, the substrate in the vapor deposition process was suspended about 2 cm above the refluxing solution in an open condensing system. Because the EG vapor had much higher density than air, it would predominantly occupy the substrate region by displacing the lighter air. In substrate region, EG vapor and water vapor were expected. Since EG was an effective reducing agent for metal ions, its vapor would not oxidize the deposited metal film. The reaction temperature (194 °C) was high enough to evaporate water which was derived from EG polyol process, and the deposition was carried out without the removal of water during refluxing. As a result, the presence of water vapor could lead to oxidation.

The SEM micrographs of FeNi films on PdGI are shown in Fig. 4. All of the films had low apparent density and the faceted Pd interface could be seen. Figs. 4 (a) and (b) show the film surfaces prepared by quenching process with the deposition time of 20 min and 60 min, respectively. It was found that the deposition took place very slowly during the first 20 min. This meant that our polyol deposition on PdGI had an incubation time. However, such incubation time was not found in the deposition on Cu substrate. This was because the electroless depo-

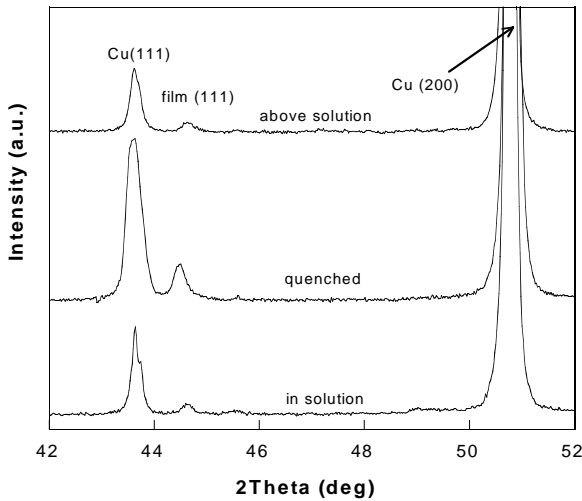


**Fig. 4.** SEM micrographs of FeNi film deposited on PdGI substrate (a) quenched with deposition time 20min; (b) quenched with deposition time 60min; (c) above solution with deposition time 60min.

sition could only occur selectively on an active surface. For the less-active PdGI substrate, self-activation by the FeNi deposits was essential for further deposition. During the incubation period, FeNi was deposited on Pd interface with very low deposition rate. When the entire surface of the substrate was well covered with deposited FeNi, the auto-catalytic activity of FeNi in this electroless method could enhance the rate of film deposition. Fig. 4(c) shows that the vapor-deposited particles occurred on the Pd and a larger porosity between the faceted particles as compared to that of solution deposition. These results showed that during quenching, the EG solution could diffuse into the voids among the faceted Pd particles and lead to FeNi deposition, thus resulting in a less porous film.

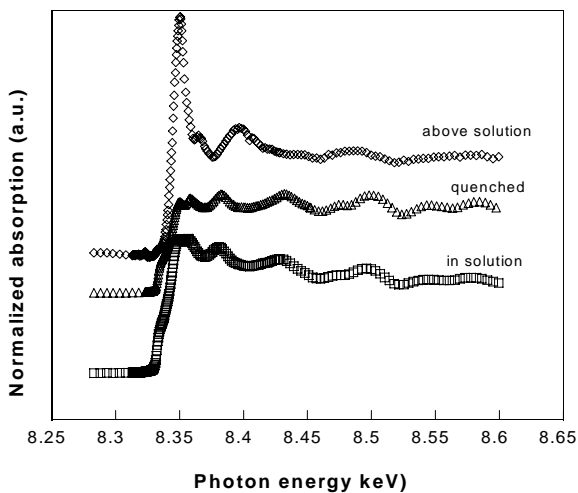
**Structure.** The information of long range order of the crystalline films were investigated using XRD.  $\theta$ -2 $\theta$  XRD results of films deposited on Cu substrates are shown in Fig. 5. Except the peaks of Cu (111)  $2\theta = 43.6^\circ$  and (200)  $2\theta = 51.7^\circ$ , only one peak corresponding to FeNi alloy was observed. Fe and Ni have mutual miscibility and are expected to form solid solution. The single peak in XRD results also suggested the formation of solid solution [17]. However, since the  $d$ -spacings of Ni and Fe are very close, we could not rule out the possibility of the combination of two elemental peaks due to size or strain line broadening [18].

The XRD results of PdGI substrate and deposited FeNi films were shown in Fig. 6. Because the

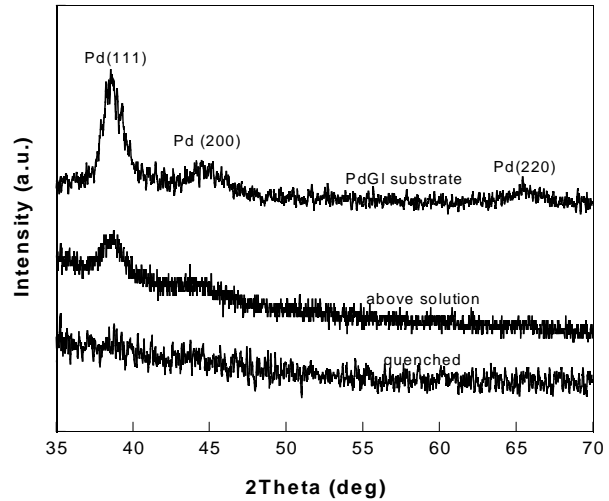


**Fig. 5.** XRD patterns of FeNi films deposited on Cu substrates. Only one film peak at  $2\theta = 44.6^\circ$  was detected.

Pd interface was very thin (25nm) and the faceted structure (average size  $3\mu\text{m} \times 3\mu\text{m}$ ) rendered the surface very rough, the XRD spectra became very noisy when using the same scanning rate as used in Fig. 5. However, the polycrystalline Pd interface could still be detected. The film grown above solution only showed one broad peak from Pd, whereas no diffraction peaks were found in quenched films. The results indicated that the films were likely to have amorphous structure. Such amorphous structure might be caused by the oxidation of films. The porous nature of the film greatly increased the surface area for oxidation to occur, resulting in amorphous oxide. It was also noted that the diffraction peaks of Pd interface disappeared in the film deposited by



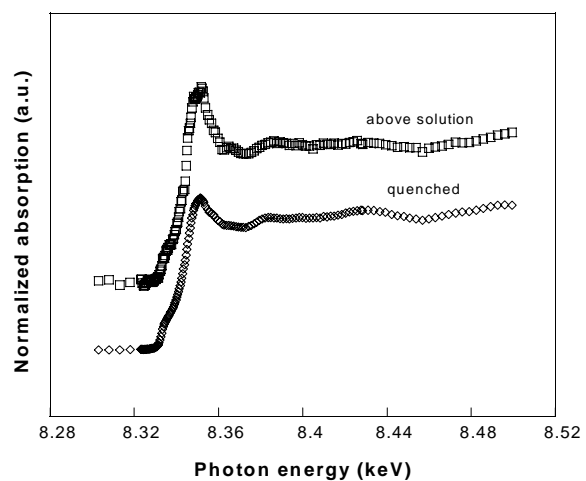
**Fig. 7.** X-ray Ni edge absorption spectra of FeNi films deposited on Cu substrate. When the substrate was suspended above solution, the sharp peak near the absorption edge (photon energy =8.35 keV) indicated Ni oxidation.



**Fig. 6.** XRD patterns of FeNi films deposited on PdGI substrates. The films were likely to have amorphous structure due to heavy oxidation.

quenching. Since the penetration depth of X-ray was several microns and the thickness of FeNi film was in the range of 400~500 nm, the disappearance of Pd peaks could not be attributed to limited X-ray penetration depth. Since Pd can alloy with Fe, the possible diffusion of Pd into deposited film is currently investigated.

The information of short range order reveals the local atomic environment i.e. nearest neighbors of a specific atom. Such average local atomic environment of as-deposited Ni and Fe was determined from extended X-ray absorption fine structure (EXAFS) data collected in fluorescence mode. Details of EXAFS study will be discussed elsewhere. Figs. 7 and 8 show the Ni edge absorption spectra



**Fig. 8.** X-ray Ni edge absorption spectra of FeNi films deposited on PdGI substrate. Both samples had been apparently oxidized.

of FeNi films deposited on Cu and PdGI substrate, respectively. The sharp peak after the edge region indicated the oxidation of Ni. It was noted that for Cu substrate, only vapor-deposited film had been oxidized, and this result was in agreement with the SEM observation. However, for PdGI substrate, both samples had been apparently oxidized. The EDX analysis of films grown on PdGI also showed high oxygen content (about 50 at.%). The oxidation of Fe and Ni led to the formation of two antiferromagnetic phases  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and NiO, which were more stable than the other oxides. As a result, the saturation magnetization ( $M_s$ ) of these films was very low and independent of Fe concentration, i.e. it was below 50 emu/cm<sup>3</sup>, whereas the  $M_s$  of FeNi alloy was 1000 emu/cm<sup>3</sup> for Fe<sub>63</sub>Ni<sub>37</sub> and 1700 emu/cm<sup>3</sup> for Fe<sub>100</sub>, respectively [19]. The ferrimagnetic phase, such as Ni ferrite (NiFe<sub>2</sub>O<sub>4</sub>) with  $M_s$  of 270 emu/cm<sup>3</sup> was not expected by simple oxidation of FeNi film.

#### 4. CONCLUSION

The polyol deposition of FeNi film on conductive (Cu) and non-conductive (Pd activated glass) substrate was studied. The film composition depended on the substrate position in the process. The solution deposition led to Ni-rich film, while the vapor deposition resulted in Fe-rich film. Films with intermediate Fe concentrations were prepared when the substrate experienced repeated sequential solution and vapor deposition. The incubation period and amorphous structure were observed when Pd activated glass was used as substrate. The film was oxidized when the vapor phase deposition process was used.

#### ACKNOWLEDGMENT

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