Photosynthesis and structure of electroless Ni–P films by synchrotron x-ray irradiation

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The authors describe an electroless deposition method for thin films, based on the irradiation by an x-ray beam emitted by a synchrotron source. Specifically, Ni–P films were deposited at room temperature. This synthesis is a unique combination of photochemical and electrochemical processes. The influence of the pH value on the formation and structural properties of the films was examined by various characterization tools including scanning electron microscopy, x-ray diffraction, and x-ray absorption spectroscopy. Real time monitoring of the deposition process by coherent x-ray microscopy reveals that the formation of hydrogen bubbles leads to a self-catalysis effect without a preexisting catalyst. The mechanisms underlying the deposition process are discussed in details. © 2007 American Vacuum Society. [DOI: 10.1116/1.2731349]

I. INTRODUCTION

Electroless deposition of Ni–P films find extensive applications in diverse fields such as the electronics, medical, aerospace, automobile, oil, and gas industries since they can be grown on substrates of many different materials and with complicated shapes, can be easily processed, and exhibit excellent resistance to corrosion, oxidation, and wear.^{1,2} Specifically, Ni–P alloy coatings with high P content (>9 wt. %) possess superior properties such as low internal intrinsic stress and nonmagnetism and have been widely employed in data storage industry.^{3,4} Recently, Ni–P plating was also employed in nanofabrication of optical devices⁵ and functionalization of carbon nanotubes.⁶

However, conventional electroless Ni–P deposition technology presents some critical limitations that hinder the fur-

ther development of Ni–P plating. In typical nickel electroless deposition procedures, an operating temperature of 90–95 °C is needed, which is unfavorable for *in situ* control and may also cause substrate damage in some cases. Furthermore, for nonconducting substrates, activation by palladium coating is required to initiate metal deposition and to improve the film adhesion.

Even though many reports provided insights about the chemical and physical aspects, the mechanisms of electroless Ni–P deposition are not yet completely understood.^{7–9} The process is complicated by factors such as (1) multiple elements (precursor, reducing agent, complexing agent, etc.) in the multistep chemical procedure, (2) formation of intermediate phases and the consequent phase transformations, and (3) the fact that incipient Ni–P clusters can act as catalysts and active nucleation sites for further self-catalytic deposition. This catalytic effect not only causes fast growth, as achieved in the present study using synchrotron radiation,

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but it also opens the way to a new class of catalytic approaches and manipulations for photochemistry.

Ionizing radiation is well known to reduce metal ions in aqueous solution systems. The formation of metallic nanoparticles and deposition coatings in solution simulated by γ -ray^{10,11} and x-ray^{12–14} irradiations provide an alternate way to obtain submicron-size films. The advantages of this approach include room temperature operation, the possible use of nonconductive substrates with minimum pretreatment, and no preformed catalyst addition. Recently, radiation-irradiation, specifically synchrotron x rays were used for Ni-P depositions.^{15–17} The influence of the temperature and of the pH value on the nucleation density of the Ni-P films were studied. The correlation between P content and structural and magnetic properties of Ni nanoparticles was also analyzed. However, limited information is available on the effects of the pH value on the morphology, structure (long- and short-range orders), and properties of the Ni-P coating. Furthermore, the detailed mechanisms of the x-ray promoted Ni-P film deposition process were not yet analyzed.

In the present work, we investigate the influence of the pH value (5–8) on the formation, surface morphology, structure, and adhesion properties of Ni-P films. We also clarify the radiation-electrochemical mechanisms of our deposition method with specific emphasis of the observed autocatalytic effect.

II. EXPERIMENT

A. Electroless Ni-P film deposition

A (100) *n*-type silicon wafer was used throughout the experiments. The substrates were cleaned by standard procedures including rinsing using a mixed solution of sulfuric acid and hydrogen peroxide with a volumetric ratio of 3:1 for 10 min and de-ionized water for 5 min. Our silicon substrates were not subject to pretreatments such as sensitization and activation in this study. De-ionized water (18.2 M Ω cm) (Millipore, Milli-Q, MA) and analytical grade chemicals were used to prepare the electroless nickel solution. The plating bath consists of 26 g l⁻¹ nickel sulfate, 30 g l⁻¹ sodium hypophosphite, 20 g l⁻¹ ammonium chloride, and 30 g l⁻¹ sodium acetate. Sodium hypophosphite acted as the reduction agent and sodium acetate as the complexing agent. The solution pH was adjusted to 4, 5, 6, 7, and 8 by diluted HCl and NaOH. The electrolyte solutions were put into well cleaned 500 ml Pryrex® beakers and transferred for x-ray exposure. The deposition processes were performed at room temperature. The radiation source is a high brightness superconducting wiggler light source at the beamline BL01A of the 1.5 GeV and 200 mA storage ring at NSRRC (National Synchrotron Radiation Research Center), Hsinchu, Taiwan, using an unmonochromatized “white” beam.¹⁸ Complementary tests were performed at the ICPCIR (International Consortium of Phase Contrast Imaging and Radiology) (7B2) beamlines of the Pohang Light Source (PLS) in Korea. The calculated photon flux¹⁹ delivered from the beamline is as shown in Fig. 1(a). The incident photons were peaked at

FIG. 1. Photon flux distribution as a function of photon energy: (a) derived white x rays at BL01A in NSRRC; (b) photon flux distribution at exposure position: for precursor solution (i) and immersed silicon substrate (ii).

around 6.2 keV and over 1×10^{12} photons/s per 0.1% bandwidth in the energy range between 1 and 30 keV. The curve (i) in Fig. 1(b) shows the estimated photon energy distribution at the exposure position including those modifications on absorption from the windows, air, and wall thickness of solution-containing beaker. The absorbed energy density by the silicon substrate which was immersed in precursor solution located at the center of the beaker is described in curve (ii) in Fig. 1(b). X-ray microscopy was used to monitor the reaction of the Ni-P solution in real time during the x-ray irradiation. For this setting up, a Teflon cell was designed and implemented for *in situ* observation with two windows sealed by thin Kapton® films.

B. Ni-P film characterization

The as-deposited films were observed by a field emission scanning electron microscope (S-4200, Hitachi, Japan). The chemical composition was analyzed by energy dispersive spectroscopy (EDS). X-ray absorption spectroscopy (XAS) measurements were performed at the 17C Beam Line at NSRRC. The data were collected in fluorescence mode at room temperature under ambient atmosphere. The crystalline character of the Ni-P alloy films was investigated by x-ray diffraction (XRD) with a Philips X'Pert system.

Adhesion test was performed with a Romulus 3 Universal Tester. The aluminum pull stud was connected by epoxy to the Ni-P plated silicon substrate and then cured at 150 °C for 90 min. The diameter of the nail head of the pull stud was 0.057 cm. The adhesion strength was calculated by dividing the exerted force to pull the film off the substrate by the bonded area of the stud nail head. At least five adhesion measurements were performed for each specimen.

III. RESULTS AND DISCUSSION

A. Film formation

Several parameters affect the formation and deposition rate of nickel particles, as revealed by the analysis of dark precipitate—including the pH value of electroless solution, exposure time, and beam current of storage ring. For example, after a short irradiation of 50 s at a storage beam current of 189.84 mA, the nickel precipitation on immersed substrates occurred in the electroless solution with a pH value of 8. For exposures with a similar beam current and a pH value of 7, a longer exposure time (140 s) was necessary to trigger the electroless reaction. Furthermore, for pH values of 5–6, as the electron beam current increased from 173.71 to 182.88 mA, the required irradiation time decreased from 550 to 280 s.

During x-ray exposure, the Ni-P film formation started from the irradiated region crossing the beam path. We also found that, after the solution exposure to the synchrotron source ended, the electroplating reactions spontaneously proceeded, extending to all the available plating surfaces including the inner wall of the beaker and the other side of the silicon substrate. The end of the autocatalytic deposition was indicated by the facts that both the inner walls of the beaker and the silicon substrate were completely coated and that the electrolyte solution became colorless with a suspension of black particulates. This revealed the autocatalytic nature of the Ni-P electroless deposition, as will be discussed later.

The pH value of the electroless Ni solution dropped with the exposure time during the deposition, as shown in Fig. 2. According to the mechanisms and the rule of charge balance that will be discussed later, this pH decay is closely related to the increase in H^+ ions and to the decrease of Ni ion concentration during the Ni-P reduction process. This phenomenon is well understood for electroless deposition either at elevated temperature^{20,21} or during exposure to x ray.¹⁶

The observed dispersed H_2 bubbles originated from the intersection region of beam and substrate. However, after a certain time of exposure, the bubbles spread to all the interface-generated volumes. In addition, it was found that the rate of hydrogen bubble evolution increased with the solution pH . In particular, solutions with pH values of 7 and

FIG. 2. Variations of the pH value of a Ni electroless solution as a function of the exposure time.

FIG. 3. Thickness and P content of the Ni-P deposition films for different pH values.

8 produced large amounts of hydrogen bubbles. This is consistent with a previous report by Borse *et al.*¹⁶

The deposition rate and the phosphorous content were both drastically influenced by the pH value. Figure 3 shows the effect of the pH value of electroless solution on the film thickness and P content. The film thickness was measured from cross-section scanning electron microscopy (SEM) micrograph and found in the range of 378–478 nm. The thickness increased with the solution pH value for a constant deposition time. It is well documented that an alkaline environment favors nickel ion reduction and therefore results in an increase of the reaction rate.^{16,22,23} The P content of all deposits was higher than 10 wt %, as revealed by EDS measurement. It was also observed that, as the pH value increased from 5 to 8, the P content decreased from 13.5 to 11.05 wt %. Such a decrease was also reported before.²¹

B. Surface morphology

Figure 4 shows the SEM images of Ni-P films formed by synchrotron x-ray irradiation for different pH values. We see that the nucleation density, the size, and the morphology of the Ni-P particles were strongly influenced by pH value variations. The surface nucleation density clearly increased with the pH value, especially when this value was raised from 4 to 5. The Ni-P particle size noticeably increased from

FIG. 4. SEM images of Ni-P films formed by irradiation with different pH values: (a) $pH=4$; (b) $pH=5$; (c) $pH=6$; (d) $pH=8$.

FIG. 5. XRD spectra of Ni-P films for different pH values: (a) pH 4; (b) pH 5; (c) pH 6; (d) pH 7; (e) pH 8.

50–60 nm to about 100–150 nm for pH values of 4–5. For pH values above 6, the size of Ni-P particles saturated to 200–300 nm.

C. Long- and short-range orders

The XRD spectra of our Ni-P films of different pH values are shown in Fig. 5. For a pH value of 4, an amorphous structure was observed. As the pH increased to 5, a tendency to a more Ni-P crystalline formation was evident. For higher pH values, one broad peak at $\sim 45^\circ$ was found, which correspond to the position of Ni (111) peak, indicating the existence of very fine Ni-P alloy crystallites. This is consistent with previous reports.^{24,25} Note that, due to the high P content in all deposits (more than 9 wt %) and to the room temperature operation, the deposited Ni-P films were amorphous. Note that in XRD characterizations, the so-called amorphous does not exclude the presence of crystallite structure. Instead, “XRD amorphous” denotes that the size of formed crystallites is too small to be detected due to significant line broadening.

Figure 6 shows the XAS spectra of Ni-P films for different pH values and P contents. Compared to metallic Ni, it is evident that the addition of phosphorous modified the local atomic environment of Ni and the effect strongly depends on the P content. For Ni-P films with $P > 10$ wt %, corresponding to pH values of 5–8, the characteristic preedge and resonances of metallic Ni gradually disappeared, indicating the formation of amorphous Ni-P alloy. In general terms, XRD and XAS give structural information on different length

FIG. 6. Near-edge x-ray absorption fine structure spectra of Ni-P films with different P contents together with standard reference.

FIG. 7. Adhesion strength of our Ni-P alloy films on silicon for different pH values.

scales. As shown in Fig. 5 and 6, the higher the pH value, the more tendency to form fine crystallites in the XAS spectra, which correlated to XRD results. We can conclude that the long-range and short-range structural characterization techniques revealed the formation of an amorphous Ni-P alloy in the deposited films.

D. Adhesion strength

As shown in Fig. 7, the adhesion strength of Ni-P films increased with the pH value from 5 to 6 and was constant for higher values. In conventional electroless deposition processes, the substrates require an activation treatment to achieve stronger adhesion. On the contrary, Ni-P deposition films prepared with our irradiation approach did not require such a substrate treatment to achieve good adhesion.

E. Mechanisms

The mechanism of electroless Ni-P deposition within the $\text{NiSO}_4\text{--NaH}_2\text{PO}_2$ system was intensively investigated. It is generally believed that the electroless metal deposition results from the anodic oxidation of reducing agent and the cathodic deposition of metal accompanied by the precipitation of phosphorous and evolution of hydrogen gas.^{7–9}

Cathodic,

Anodic,

Sodium hypophosphite (NaH_2PO_2) was used for the electroless deposition of Ni-P films mainly because of its strong reducing capability. However, hypophosphite ion (H_2PO_2^-) is stable in aqueous solution in the absence of catalytic metals such as gold, nickel, palladium, etc.²⁵ A dehydrogenation step is essential for this ion to function as a powerful reductant and this is usually achieved by adding a catalyst and

FIG. 8. Hypophosphite solution irradiated by x rays and the snapshot images after different irradiation periods taken at a speed of 2 frame/s: (a) 0.5 s; (b) 2 s; (c) 3 s; (d) 4 s; (e) 5 s; (f) 6 s; (g) 7 s; (h) 8 s; (i) 9 s; (j) 10 s.

heating the solution to a high temperature.^{26–28} This is consistent with the high activation energy ($17.7 \text{ kcal mol}^{-1}$) found for the Ni–P electroless deposition process due to the fact that the P–H chemical bond must be broken.^{7,29} Due to the irradiation by high flux of energetic x-ray photons (energy $>10 \text{ keV}$) of hypophosphite ions, bonds such as H–P, P–O, and P=O might undergo broken to various extents depending on the x-ray absorption by the involved elements.

These facts lead us to a plausible explanation of the role of irradiation in our present approach. We believe that the synchrotron x-ray photons contribute to the breaking of the covalent P–H bonds in hypophosphite ions—thereby enabling the deposition process to occur even at room temperature. To verify this hypothesis, we used x-ray microscopy to observe the reaction during irradiation. Figure 8 shows the time-resolved microradiology images of sodium hypophosphite aqueous solution. Images (a)–(j) are sequential snapshot showing the hydrogen bubble evolution during the irradiation of the hypophosphite solution. We observed that hydrogen bubbles evolved within a few seconds upon x-ray exposure.

The dehydrogenation of hypophosphite ion and the dissolution of hydrogen can be explained by the process^{26–28}

In other words, hypophosphite can be dehydrogenated by synchrotron x-ray irradiation that provides the necessary activation energy. The combination of hydrogen atoms produces hydrogen molecules and the observed hydrogen bubbles.

Another important element possibly involved in the dehydrogenation of hypophosphite ions was the presence of secondary electrons generated from the irradiated the silicon substrates. Our previous studies^{30,31} on forming patterned polymethyl methacrylate and Cu coatings on selected substrates proved the important role of interactions between incident x-ray photons and substrate materials. However, a spiking test experiment performing with a precursor solution in the absence of a substrate indicated that the substrate is not essential to produce Ni–P precipitates. Even though the possibility that secondary electrons participate in the dehydrogenation procedure cannot be excluded, its role is probably limited to accelerate the initial formation of Ni–P deposits. In addition, due to the nonspecific nature of x-ray irradiation on solutions and the existence of numerous ionized and excited species in the irradiated solution, it would be difficult to identify the contribution of individual species.

As already mentioned, after a certain time, the irradiation of the $\text{Ni}_2\text{SO}_4\text{--NaH}_2\text{PO}_2$ solution was interrupted but the Ni–P deposition continued. We contribute this phenomenon to the catalyzing action of Ni–P clusters that provide reaction sites and facilitate further Ni–P deposition. Autocatalytic behavior in the electroless Ni–P deposition process was previously analyzed^{17,32–35} in the presence of a catalyst surface. In our present study and in agreement with previous reports,^{36–38} we found that an induction period is required to create the catalyst particles before the catalytic reaction takes place. As described above, the length of the incubation decreased with the increase of the pH value solutions from 5 to 8 and also was affected by the incident photon beam conditions.

Since intensive x-ray irradiation alone is also capable to produce solvated electrons (e_{aq}^-) and H radicals from the most abundant solvent of the Ni_2SO_4 solution, thus facilitating the reduction of metallic ions, the contributions of the radiation and of the reducing agent must be distinguished from each other. In our radiation-induced chemical approach, solvated electrons, H, and OH radicals are generated by x rays.

Both the solvated electrons and H radicals are strong reducing agents so that in the following steps they easily reduce the metal ions to free metal atoms. On the other hand, OH radicals are able to oxidize the ions or atoms into a higher valence state, counterbalancing the formation of metallic clusters. Therefore, the overall reduction of Ni ions by x-ray radiation is the result of the interplay of the two conflicting processes.

Test experiments were performed to clarify the contribution of x-ray irradiation on the reduction of Ni ions. First, Ni_2SO_4 solution without sodium hypophosphite was subject to x-ray exposure for over 1 h. We observed no appreciable chemical reaction, as shown by the absence of bubble evolution and precipitation. Then, we added to the solution a certain amount of secondary alcohol (2-propanol) that acts as OH radical scavenger. After a short x-ray exposure, dark precipitates were observed that were identified as Ni-P particulates. When the Ni-P deposition is implemented in the absence of OH radical scavengers, the contribution of the x-ray radiation to reduction of Ni ions is very limited. By comparing the chemical bond energy of H-O in the water molecule and H-P in the hypophosphite ion, we conclude that the H-P bond is easier to break by x-ray irradiation. Therefore, the free radicals produced by the dehydrogenation of hypophosphite ion are likely to dominate the electroless deposition of Ni-P.

The overall mechanism of our x-ray induced electroless deposition can be summarized as follows: the interaction of x-ray photons and hypophosphite ion produces hydrogen radicals and HPO_2^- radicals. Even though these hydrogen radicals cannot reduce all divalent Ni ions to metal atoms, a portion of the formed Ni acts as catalyst, activating an autocatalytic deposition mechanism. Consequently, large quantities of Ni-P clusters are produced even without further x-ray irradiation. In essence, the role of x ray is limited to supplying the activation energy for the dehydrogenation reaction of NaH_2PO_2 that then triggers further electroless Ni-P deposition.

IV. CONCLUSIONS

Ni-P films were deposited at room temperature on non-pretreated silicon substrates by irradiating the electroless solution with synchrotron x rays. The synthesized films were amorphous and their formation, structure, and properties were strongly influenced by the pH value. We propose a simple model for this process: x-ray irradiation triggers the dehydrogenation of hypophosphite ion by providing the activation energy and therefore giving rise to a radiation-chemical process. After the appearance of incipient Ni-P clusters produced by the reduction of Ni ions with hydrogen radicals, the electroless Ni-P deposition continues spontaneously by self-catalysis.

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