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Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Effect of synthesis conditions and post-deposition treatments on composition and structural morphology of medium-phosphorus electroless Ni–P films

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ARTICLE INFO

Article history:

Received 31 August 2010

Accepted in revised form 14 March 2011

Available online 29 March 2011

Keywords:

Electroless deposition

Scanning electron microscopy

Ni–P thin films

Post-deposition treatment

Atomic force microscopy

ABSTRACT

The optimized plating bath composition (mol%) of 0.47NiCl₂:0.23NaH₂PO₂:0.13C₄H₄Na₂O₄:3.47NaCl:95.70H₂O produced Ni–P films with ~10 wt.% P at 85 °C over copper and steel substrates. The presence of chloride ions (Cl[−]) in the plating solution was found to facilitate initial deposition without any need of surface activation. Film growth rates as high as 7–8 μm/h were achieved with minimal or no deposition on surfaces other than the substrates. Scanning electron microscope (SEM) and atomic force microscope (AFM) studies revealed cauliflower-like morphology with submicron size grains. Increasing the amount of reducing agent increased film smoothness and refined grain size with corresponding increase in P content. X-ray diffraction studies of the deposit revealed semi-crystalline nature of the film which underwent transition to fully crystalline form upon heat treatment with an associated increase in average HK value from ~390 to 807 HK. High temperature provided driving force for surface and volume diffusion that subsequently led to reduced porosity and more homogeneous composition through rearrangement of atoms to form certain Ni_xP_y phases. Acid etching of the deposits transformed shiny films into matte black surfaces due to preferential removal of nickel leading to formation of porous structure with stalagmite-like morphology.

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1. Introduction

Electroless nickel (EN) deposition is an autocatalytic chemical reduction process in which the reducing agent is oxidized and nickel ions are deposited (reduced) onto a substrate. Once nickel monolayer is produced, it acts as a catalyst for subsequent process. This technique is widely used in modern industry to address applications involving improved wear and corrosion resistance, higher hardness, and tunable electrical and magnetic properties [1,2]. It is advantageous over electrochemical deposition technique in terms of no external current source requirement, film thickness uniformity, and adaptability for uniform coating on complex shapes as well as non-conductive substrates. Typical bath constituents used for EN film deposition are metal salt, reducing agent, complexing agent and water. Other additives such as stabilizer and brightener may also be used to obtain desirable deposit characteristics. Almost exclusively, nickel sulfate has been used as the source of Ni²⁺ ions [3,4]. Although the effect of halide ions on substrate surface activation, deposition rate, and microstructures of the films produced was investigated [5,6], the use of nickel halide salts as a source of both metal ions for film deposition and halide ions for substrate surface activation has not been explored.

Factors such as type and concentrations of the reducing agent and stabilizer used, bath pH and the deposition temperature influence deposition rate, properties of coated components and the structural behavior of deposits. Using PdCl₂ and SnCl₂ for surface sensitization, kinetics of film formation and growth for different temperatures and bath pH values were investigated [7]. Increasing the amount of complexing agent in plating bath was reported to alter the film morphology from hemispherical to planar microstructure [8]. The bath chemistry can be modified and surface activation carried out to obtain deposits on diverse substrates such as magnesium and its alloys [9,10], titanium [11], carbon fibers [12], and carbon nanotubes [13,14].

Through control of bath chemistry and deposition conditions, morphology, composition, and in turn, physical properties of the deposited films can be tailored. Post-synthesis treatments such as heat treatment and acid etching can be employed to modify film characteristics. Whereas the former may lead to film densification and crystallization, the latter treatment produces surfaces with different pore morphologies useful for certain practical applications [15,16].

In this work, nickel chloride being the most common halide-based nickel salt was used for formulating bath for EN deposition. Preliminary experimentation addressed optimization of bath composition and deposition conditions. Once bath formulation was optimized, the effect of bath composition and plating temperature was assessed. Then, using films produced from optimized bath composition, the effect of heat treatment and acid etching on composition, surface morphology, and hardness values was examined.

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2. Materials and methods

Nickel chloride (NiCl_2), sodium hypophosphite (NaH_2PO_2), sodium succinate ($\text{C}_4\text{H}_4\text{Na}_2\text{O}_4$), and sodium chloride (NaCl), all in hydrated form, were used as metal ion source, reducing agent, complexing agent, and surface activation agent, respectively. All the chemicals were of analytical grade. To optimize bath composition for reasonable deposition to occur, the amount of NiCl_2 , NaCl , and sodium succinate was varied to investigate the effect of solution chemistry on deposition behavior. Initially, only NiCl_2 was used as chloride (Cl^-) ion source. In later experiments, NaCl was also added as a source of Cl^- ions.

Copper, mild steel, and stainless steel substrates were used for this work. For each substrate, small coupons $25 \times 25 \times 3$ mm in size, were sectioned and prepared by grinding on successively finer grades of SiC paper down to 1200 grit size and then polished with 6, 3, and 1 μm diamond paste. After polishing, the substrates were ultrasonically cleaned in ethanol followed by rinsing with deionized water and blow drying. The deposition was carried out at 85 $^\circ\text{C}$ for 1 h by immersing the substrate into agitated bath.

Heat treatment and acid etching of the as-deposited films were carried out as post-synthesis treatments to study compositional and morphological changes in deposits. The films were heat treated at 400 $^\circ\text{C}$ for 1 h under atmospheric conditions. In some cases, the as-deposited films were treated with 4.0 and 10.0 M HNO_3 solutions for different times to obtain different pore morphologies.

Both as-deposited and treated films were characterized using various characterization tools. Surface topography, cross-sectional morphology of the films and elemental composition of the deposits were examined under scanning electron microscope (JEOL JSM6490). Compositional analysis of the as-deposited and heat treated films was performed using x-ray diffractometer (XRD STOE65022). Surface topography of the as-deposited and etched films was also investigated using atomic force microscope (JEOL SPM5200). Hardness data for the as-deposited and heat treated films were obtained from Knoop microhardness tester (Shimadzu HMV-2).

3. Results and discussion

The solution chemistry plays a critical role in determining the extent of film deposition. Depending on the relative molar content of metal source, reducing agent, and complexing agent in the plating bath, the solution can be either very stable that no deposition occurs or so unstable that instantaneous precipitation in the solution takes place. Several bath formulations were tried before significant deposition on substrate surface was noticed. In addition to NiCl_2 , sodium chloride (NaCl) as a source of chloride ions (Cl^-) was explored for surface activation. Once process control was improved, the efficiency of coating (which is the amount of adherent nickel deposited onto substrate in a fixed time expressed as a percentage of the total metallic nickel recovered from bath solution) significantly increased owing to bath circulation and homogeneous bath temperature. A series of experiments were performed with different bath compositions to assess electroless deposition behavior. Using sodium hypophosphite and sodium succinate as the reducing agent and complexing agent respectively, nickel chloride and nickel sulfate was explored as metal salts. Also, plating solution without and with different amounts of sodium chloride was used to examine kinetics of film deposition. Such experimentation led to an optimum bath composition of (by mol%) 0.46 NiCl_2 , 1.37 NaH_2PO_2 , 0.12 $\text{C}_4\text{H}_4\text{Na}_2\text{O}_4$, 3.47 NaCl , and 94.61 H_2O . Unless otherwise stated, the same composition was used for all experiments.

In the absence of a suitable stabilizer to maintain certain value of bath pH, the change in bath pH as a function of time was investigated for temperatures of 80, 85, and 90 $^\circ\text{C}$. The trends observed are presented as pH versus time curves in Fig. 1. Generally, the plating solutions had an initial pH value of ≥ 5.7 which dropped to less than 4.0 in about 2 hour time. For each temperature, the plating bath pH was constant for

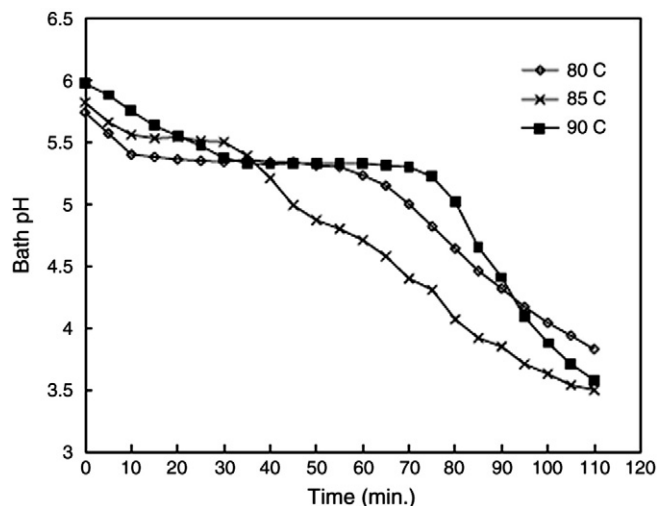


Fig. 1. Change in bath pH with time for deposition temperatures of 80, 85, and 90 $^\circ\text{C}$.

sometime, as indicated by the presence of a plateau in each curve. Electroless nickel deposition carried out on substrates for certain range of pH values revealed that highest deposition rate of 11 $\mu\text{m}/\text{h}$ was observed for pH values in the range of 5.20–4.72. As the plating bath became more acidic from an initial value of 5.50, the film deposition rate initially increased drastically followed by a small, continuous decrease. This finding may be attributed to the protons coming from the reducing agent. It is an established fact that more acidic baths result in deposits with higher phosphorus content [7]. Nevertheless, the gradual drop in deposition rate is due to replenishment of Ni^{2+} ions in the plating solution. Although the increase in temperature resulted in more smooth films, the plating temperature was chosen to be 85 $^\circ\text{C}$ to avoid instantaneous decomposition of plating solution at elevated temperatures [17]. Also, there was an associated transformation from dull to lustrous visual film appearance upon increasing the temperature.

The effect of concentration of reducing agent on deposit properties was assessed. Theoretically, one each of Ni^{2+} ion and H_2PO_2^- radical are obtained from NiCl_2 and NaH_2PO_2 molecules, respectively, the $\text{Ni}^{2+}/\text{H}_2\text{PO}_2^-$ ratio in the standard solution is 0.33. Fig. 2(a) shows that the resulting deposits exhibited two distinct surface morphologies, providing insight into the film growth mechanism. At the initial stage of film growth, nucleation of sub-micron size (~ 350 – 550 nm) clusters occurred on the substrate surface. The growth stage overlapped with nucleation step, resulting in deposit densification as manifested by the presence of large, round globular features. The average size of these globular clusters was of the order of a few microns. Despite a certain degree of densification during film growth, both surface and volume porosities were nevertheless seen in the overall deposit structure, originating from a combination of high film growth rate and hydrogen evolution at the film surface. Such deposit morphology necessitated the introduction of a post-deposition heat treatment step for further densification and recrystallization (discussed later in this paper). As compared to the standard bath composition, a solution with an increase in reducing agent concentration by six-fold produced deposits with more smooth morphology and an average cluster size in the submicron size regime, as shown in Fig. 2(b). A much higher concentration of reducing agent, as in this case, has deleterious effects on bath stability, and deposit composition due to high concentration of phosphite anions in the solution that eventually leads to precipitation of nickel phosphite in the solution. There was also an accompanying increase in phosphorus incorporation into the deposit to 14 wt.% against a value of ~ 10 for standard bath composition, as revealed by the EDS analysis. This increase in P content can be attributed to a series of intermediate reactions [18] eventually leading to phosphorus reduction and subsequent incorporation into the growing film. The film morphology and growth rate were

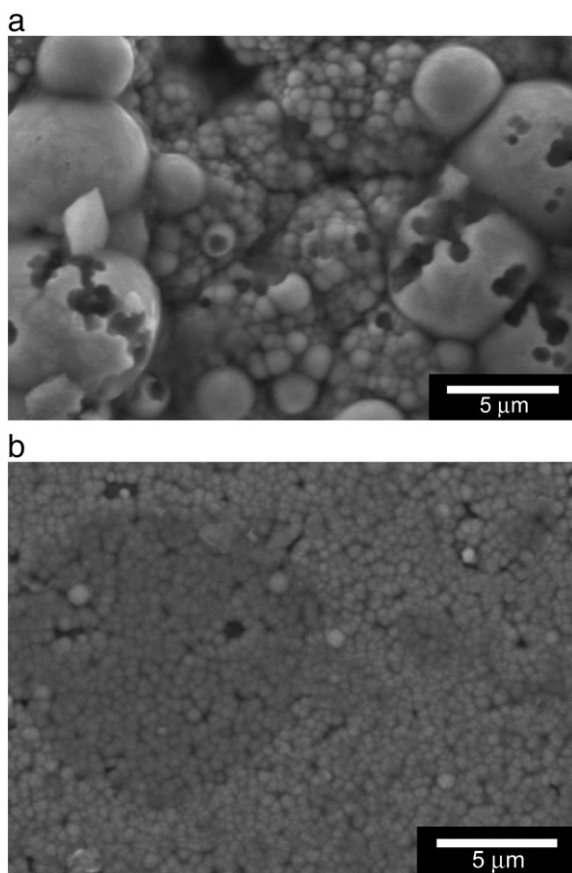


Fig. 2. Effect of reducing agent content in the bath solution on resulting film morphology for $\text{Ni}^{2+}/\text{H}_2\text{PO}_4^{2-}$ ratio of: (a) 0.33, and (b) 2.00.

similar for copper, mild steel, and stainless steel substrates. In other words, the type of substrate surface did not appear to significantly influence deposit characteristics.

Heating the films to 400 °C for 1 h under atmospheric pressure resulted in consolidation of the deposited films, as evident from SEM results shown in Fig. 3. Upon heat treatment, the film became relatively smooth with fewer cauliflower-like features. Also, the degree of surface porosity was found to have been significantly reduced. In addition to modification in deposit structure and morphology, the heat treatment cycle also induced re-crystallization in films, as presented by X-ray diffraction spectra in Fig. 4. The as-deposited films were semi-crystalline in nature as evident from Fig. 4(a) where peaks are not only broad with high background noise signal, but also sharp to some extent indicating some degree of crystallinity. The peaks in the spectrum were indexed to be due to pure Ni and various phases such as $\text{Ni}_{2.55}\text{P}$, Ni_5P_2 , Ni_7P_3 , and Ni_5P_4 . After heat treatment, more peaks appeared on the spectrum suggesting film transformation from predominantly amorphous to a crystalline deposit. It is proposed that the heat treatment cycle caused precipitation of various nickel phosphide (Ni_xP_y) phases within the deposit. Generally, the order of peak intensity was found to decrease for phases with gradually more P content in the resulting phase. An associated increase in average hardness value of the deposit upon heat treatment was also observed. As shown in Fig. 5, the average value of Knoop hardness number almost doubled upon heat treatment of the as-deposited film. The measured average value of ~807 HK (equivalent to HV 775) is below the maximum reported value of 916 HK [19] for Ni–P films with moderate phosphorus content, thus suggesting that the heat treatment cycle maybe further tuned to obtain even higher HK values.

Upon acid etching, the metallic semi-bright surfaces of the as-deposited films transformed into black spectrally selected surfaces owing to selective etching thus resulting in a porous network. The

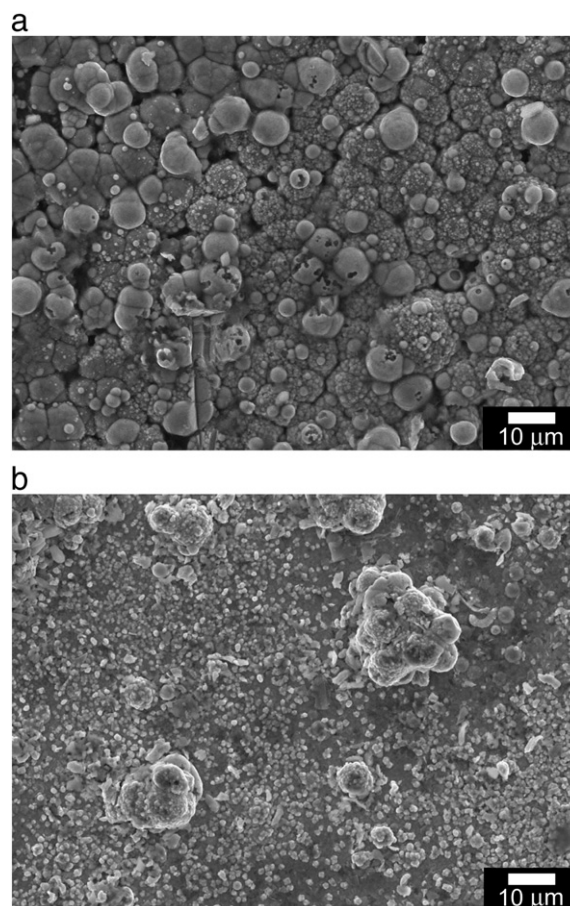


Fig. 3. Low magnification SEM micrographs presenting the effect of heat treatment on deposit morphology before (a) and after heat treatment (b).

pore morphology appeared to be stalagmite-like [15] with an average pore size in the submicron range. The EDS analysis of the etched surface confirmed preferential etching of the film with elemental composition (by wt. %) of 83Ni–17P. The average surface roughness of

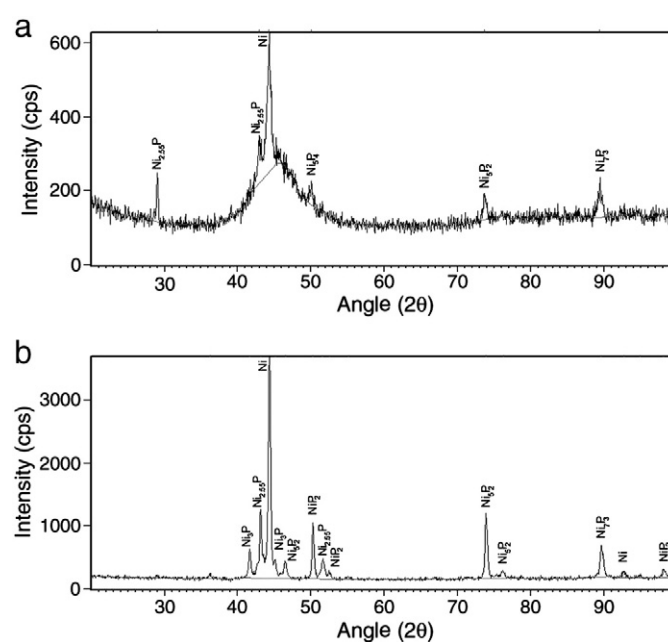


Fig. 4. X-ray diffraction spectra of the as-deposited (a) and heat treated (b) films.

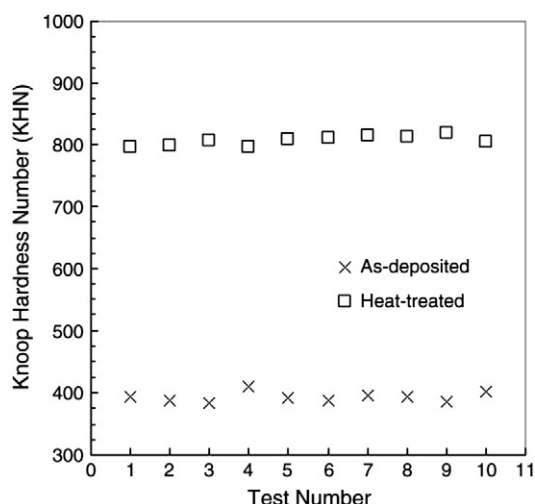


Fig. 5. Graphical representation of Knoop hardness test data for as-deposited and heat treated films.

the partially and completely etched films is manifested by 3-D topographical images of the AFM microstructures, as shown in Fig. 6. Whereas partially etched films exhibited a maximum surface roughness of the order of sub-100 nm, complete etching produced film surfaces with a roughness level of few hundreds of nanometers. An SEM microstructure of the etched Ni–P deposit is presented in Fig. 7. Such surfaces can be used for applications involving low optical and electron reflectances [20]. It is noteworthy, however, that care

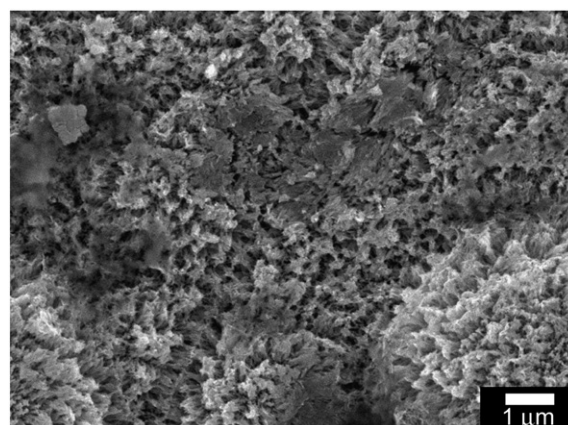


Fig. 7. SEM microstructure of the etched Ni–P film surface.

must be examined while etching as excessive etching may result in delamination of the deposit from the substrate surface.

4. Conclusions

Electroless nickel–phosphorus films with phosphorus content of ~10 wt.% were produced using optimized bath composition (by mol%) of 0.47NiCl₂:0.23NaH₂PO₂·6H₂O:0.13C₄H₄Na₂O₄·H₂O:3.47NaCl:95.70H₂O. Careful control of processing conditions such as temperature and bath circulation resulted in film growth rate of 7–8 μm/h, owing to the initial surface activation due to chloride ions present. Increasing the reducing agent content in plating bath resulted in more smooth films with greater extent of phosphorus incorporation into the deposits. The semi-crystalline, porous nature of the as-deposited films can be modified to dense, fully crystalline deposits with a 100% increase in hardness level with HK values of 390 and 807 HK, respectively. Heat treated films can be used for applications where excellent mechanical properties such as wear and abrasion resistance, hardness, etc. are required. Acid etching of the as-deposited films produced matte black surfaces due to preferential removal of nickel from deposit. Such films can be utilized in application involving high optical and/or electrical absorption.

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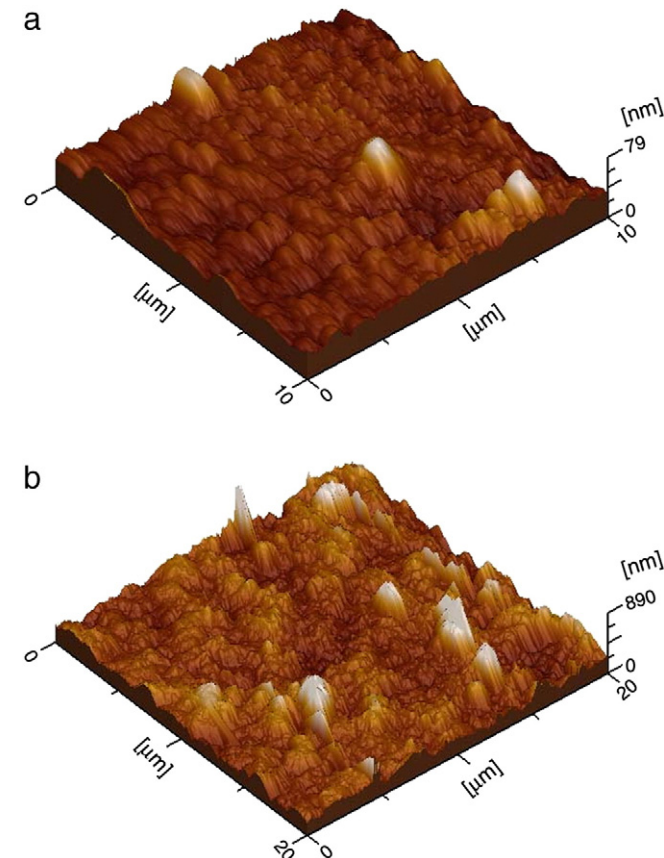


Fig. 6. AFM images of the surface topography for Ni–P films: (a) as-deposited, and (b) after complete acid etching.