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Effect of lactic acid on nucleation morphology and surface roughness of electroless Ni–P deposition in nanoscale

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Abstract. **The present work aims to study effect of lactic acid concentration as complexing agent on surface roughness and nucleation morphology of electroless N–P deposition. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) have been used to study nucleation morphology and surface roughness of deposition. Deposition process started at some initial priority growing centres independently distributed on the substrate. We found that the morphology and surface roughness of deposition strongly depends on the complexing agent concentration. Morphology of initial deposited centres with no concentration of lactic acid was in coniform structure. By increasing the complexing agent concentration, the structure of initial growing centres changed from coniform to nodular shape and the surface roughness of depositions decreased.**

Keywords. **Electroless; complexing agent; surface roughness; nanoscale; morphology; AFM; SEM.**

1. Introduction

Electroless deposition technique of Ni–P alloy coating has been a well known commercial process which has found numerous applications in many fields due to its excellent properties of coatings such as high corrosion resistance, high wear resistance, good lubricity, higher hardness and acceptable ductility (Changdong *et al* 2005; Balaraju *et al* 2007; Palaniappa and Seshadri 2007). The applications of electroless Ni–P deposit include the fabrication of components for the automotive, oil and aircraft industries and manufacturing of electronic and computer equipment (Winowling Jappes *et al* 2005) Ni–P binary alloys are prepared by autocatalytic method using nickel sulphate or nickel chloride as a nickel source and hypophosphite as a reducing agent along with complexing agent, accelerating and buffering agents (Takács *et al* 2007). Electroless Ni–P deposit is a self-initiating autocatalytic process where nickel ions in an aqueous solution are chemically reduced and plated on a catalytically active substrate with continued Ni deposition through the catalytic action of deposition (Balaraju *et al* 2006). Although electroless deposition processes have been studied for over a century, little is known about the role of nucleation morphology on surface roughness of deposition. Homma *et al* (1991) have shown that at the initial deposition stage, the electroless Ni–P deposits consist of very fine crystal components that grow isotropically to form uniform and spherical grains. The nucleation of electroless Ni–P occurs at grain boundaries and surface defects on the Al substrate, coalescence of these nuclei resulting in a continuous Ni–P layer (Backovic *et al* 1976). Huang and Cui (2007) have shown that the presence of sufficient aminoacetic concentration as a complexing agent can change the initial priority growing centre structure from the coniform to planar shapes and finally changing the morphology of the deposit. Lactic acid is a rare example of an organic acid additive which acts not only as a complexant but also as a buffer (Riedel 1991). In this paper, we report a study on the nucleation and growth processes of Ni–P deposition by lactic acid as a complexing agent. The initial stages of Ni–P electroless depositions and surface roughness were studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM). We found that the nucleation morphology and surface roughness of depositions strongly depend on the complexing concentration. With increasing concentration of lactic acid, phosphor content in the deposits increases while roughness and spot sizes decrease. By increasing the content of complexing agent in the bath solution, morphology of initial deposition centres change from coniform shapes to nodular. By using very clear pictures in nano-scales these achievements are discussed.

2. Experimental

Nickel sulphate hexahydrate was used as the source of nickel. Sodium hypophosphite was used as the reducing agent,

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which also served as the source of phosphorus. Lactic acid and propionic acid were used as the complexing agents to control the rate of release of free metal ions for the reduction reaction. The chemical composition of the plating bath and its operating conditions are given in table 1.

During plating, temperature of the bath was maintained at 90 ± 5 °C and pH was maintained at 4·6 with the addition of ammonium hydroxide. In order to study initial depositing centres and nucleation morphology, the plating time was chosen as 10 s. The substrates used were (20 × 20 × 4 mm) St 37 steel sheets. Before deposition, the substrates were polished in the following sequence: 400, 600, 800, 1000, 1200, 1500, 2000 and 2500 grit polishing sheets then degreased with NaOH (150 g/l) solution at 65–70 °C for 25 min, then rinsed with deionized water. The degreased samples were deoxidized for 30 s in acidic pickling bath (30 vol. % hydrochloric acid solutions) rinsed in running and deionized water. Finally, the samples were put into the electroless solution. After plating, samples were rinsed in running and deionized water and finally dried. To investigate the surface roughness and nucleation morphology of deposits, AFM (Model SSI, CSEM) and SEM (Model SSI, CSEM) equipped with EDX were employed.

Table 1. Chemical composition of plating bath and its operating conditions.

Nickel sulphate (g/l)	21·2		
Sodium hypophosphite (g/l)	24		
Lactic acid concentration (g/l)	0 g/l	14 g/l	28 g/l
Propionic acid (g/l)	2·2		
pH	4·6		
Temperature (°C)	90 ± 5 °C		
Deposition time	10 s		

3. Results and discussion

Figure 1(a) shows SEM micrograph of electroless Ni–P deposit obtained from deposition bath without lactic acid. Although small and bright grain centres as initial Ni–P deposit can be found on the surface, the main microstructure of St37 substrate is almost visible. SEM micrograph of electroless Ni–P deposit with 14 g/l lactic acid has been shown in figure 1(b). Main microstructures of substrate St37 disappeared completely and a rough layer of electroless Ni–P

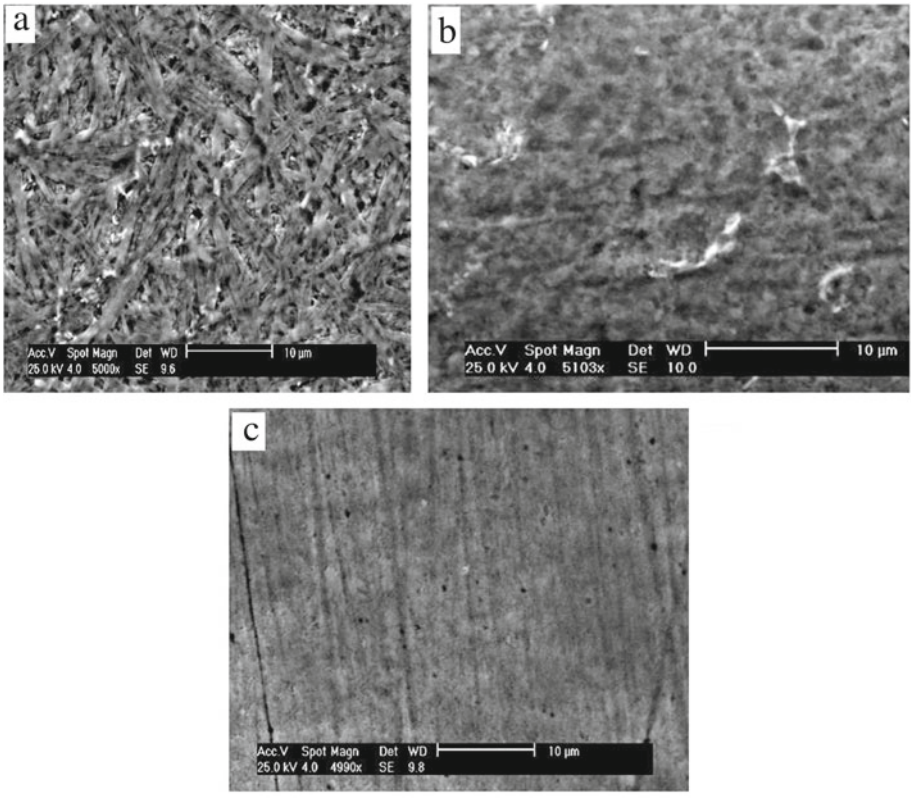

Figure 1. SEM micrographs of electroless Ni–P deposit obtained from deposition bath without lactic acid (**a**), with 14 g/l lactic acid (**b**) and with 28 g/l lactic acid (**c**).

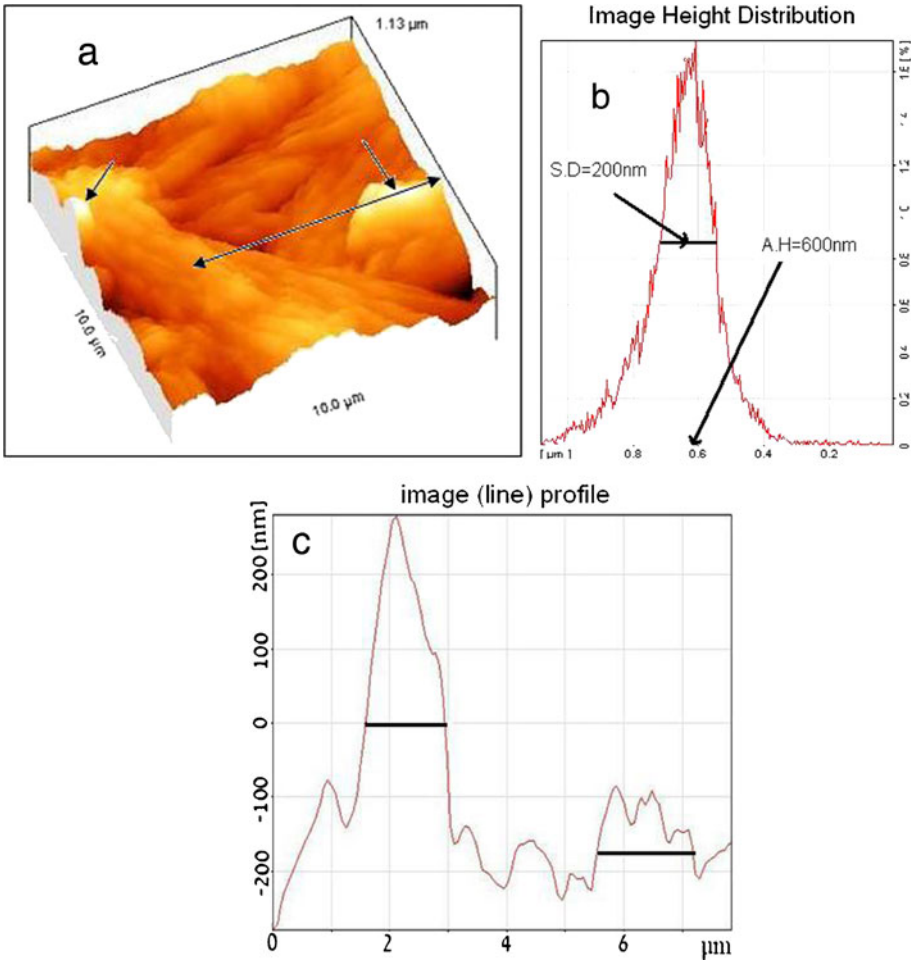

Figure 2. AFM images of deposits without lactic acid (**a**), average surface roughness distribution (**b**) and image profile along a line (**c**).

deposit covered the entire surface. Increasing lactic acid concentration to 28 g/l changed the surface morphology of deposits from a rough layer to a smooth layer as seen from figure 1(c).

AFM images of deposits with different concentrations of lactic acid are shown in figures 2 through 4. Figure 2a shows the initial Ni–P growing centres in coniform structure on the surface (arrows) with no concentration of lactic acid. Average surface roughness distribution from figure 2b is evaluated as ∼600 nm with standard deviation of 200 nm. Figure 2c shows image profile along a line. The diameter of spots is in the 1400–1600 nm range.

Figure 3a shows AFM image of deposit with 14 g/l lactic acid concentration. As seen from the image, the surface has been completely covered with several high regions as coniform structure and low regions as crater structure. Initial Ni–P deposits in coniform structure seem to be consisting of some agglomerated nodules. Average surface roughness of deposit was evaluated as 280 nm with a standard deviation of 150 nm (figure 3b). The diameter of spots is in the 200–1000 nm range.

Figure 4a shows AFM image of deposit with 28 g/l lactic acid concentration. Deposit with 28 g/l lactic acid concentration showed a nodular-like structure with a few coniform regions. Average surface roughness of deposit was evaluated as 100 nm with a standard deviation of 100 nm (figure 4b). The diameter of spots is in the 100–200 nm range (figure 4c).

It can be seen from table 2 that the average height (roughness) of initial deposition centres, standard deviation and spot sizes decrease as lactic acid concentration increases from 0 g/l to 28 g/l. With increase of lactic acid concentration from 0 g/l to 28 g/l, coniform structures changed to nodular structures (see figures 2a, 3a, 4a and table 2).

When sufficient lactic acid was added to the bath deposition, it combined mostly of the free nickel ions so mostly of initial deposited self-catalyzed points were occupied by P

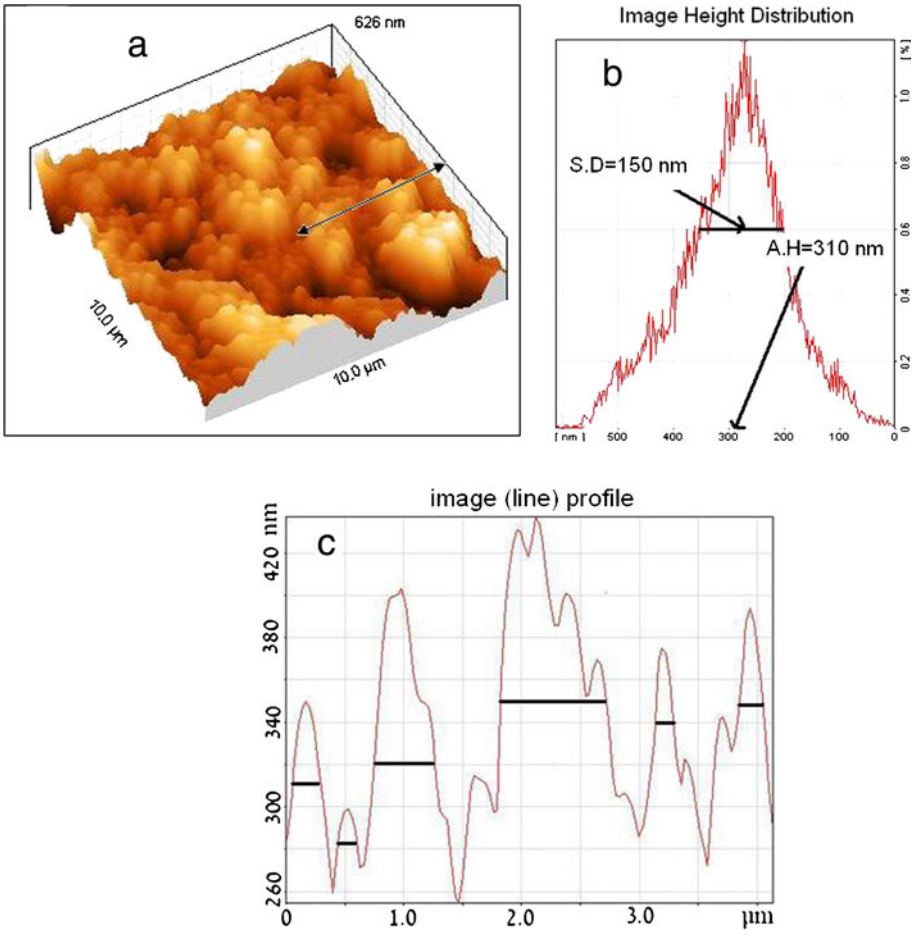

Figure 3. AFM images of deposits with 14 g/l lactic acid (**a**), average surface roughness distribution and (**b**) image profile along a line (**c**).

atoms. It can be said that the addition of lactic acid changes the direction of growth of initial priority and the structure of initial deposits. Indeed the direction of priority growth has been changed from vertical to cross type. Priority cross growth affects the deposition growing centres and gradually changes their morphology from the coniform to the nodular shapes. Coniform shapes form a rough morphology and nodular shapes form a smooth morphology.

These results indicate that lactic acid concentration in the composition bath is very important and it strongly affects the morphology and surface roughness of deposits.

Figure 5 shows the P content in the deposits. We can see that P content in the deposits rises with increasing concentration of lactic acid.

The reaction between complexing agent and metal ion at electroless Ni–P deposition can be described as (Huang and Cui 2007).

$$ML^{z-n} = M^{+z} + L^{-n}, \tag{1}$$

where ML^{z-n} denotes the metal complex, M^{+z} the "free" ions and L^{-n} the "free" complex. When complexing agent is added to the deposition bath, equilibrium was established between nickel ion and complex.

The partial cathodic reaction can be expressed as (Riedel 1991):

$$Ni^{2+} + 2H_{ads} = Ni + 2H^{+}, \tag{2}$$

$$H_2PO_2^{-} + H_{ads} = H_2O + OH^{-} + P. \tag{3}$$

It is apparent from (1) and (2) that when complexing agent concentration increases in the composition bath, the free H_{ads} concentration increases. Higher concentration of H_{ads} promotes higher content of phosphorus in deposit (3). When P content increases in deposit most of P atoms drop around the nickel self-catalyzed points, reducing the vertical priority growth, promoting the cross priority growth of the initial nucleation.

Table 2. Average height (roughness), standard deviation and image profile of initial deposition centres.

Lactic acid concentration (g/l)	Average image roughness (nm)	Standard deviation (nm)	Image profile (spot sizes) In (nm)	Nucleation morphology
0	600	200	1400–1600	coniform
14	280	150	200–1000	coniform
28	100	100	100–200	nodular

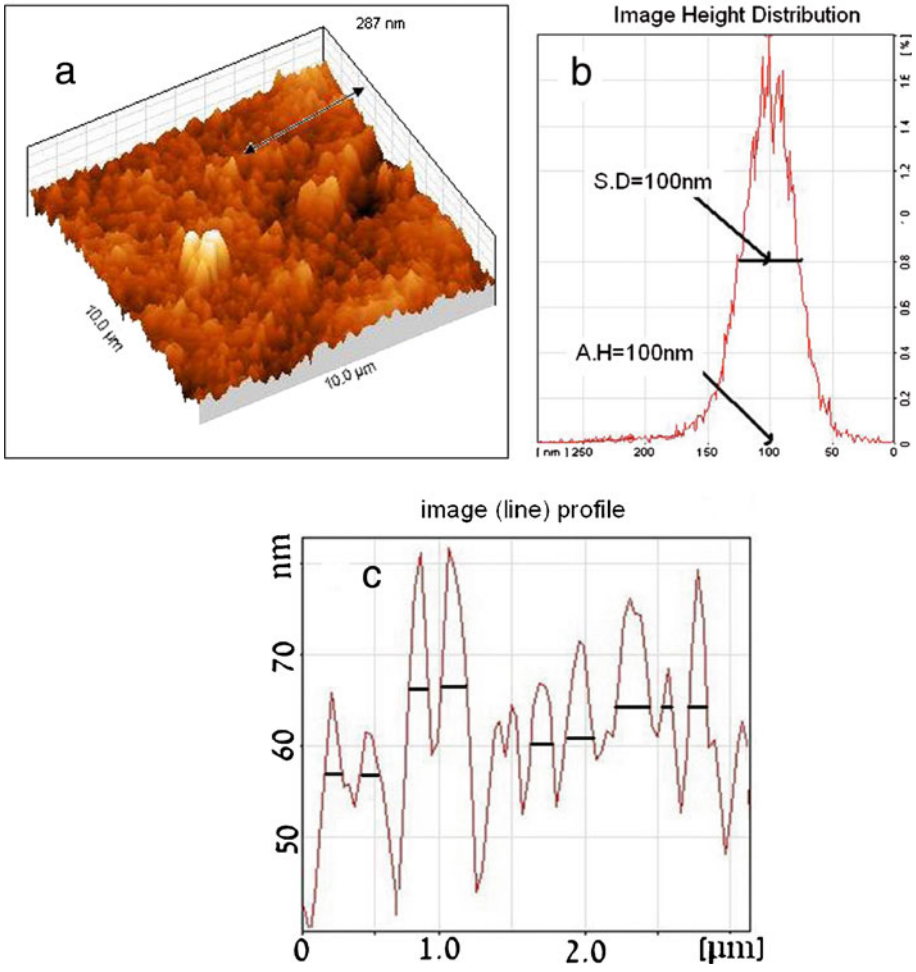

Figure 4. AFM images of deposits with 28 g/l lactic acid (**a**), average surface roughness distribution (**b**) and image profile along a line (**c**).

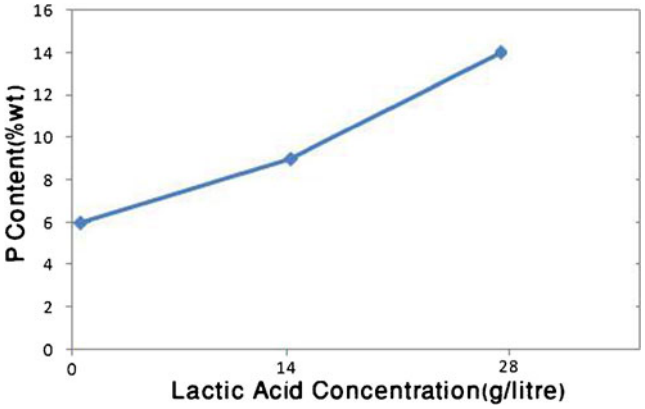

Figure 5. P content in deposits.

4. Conclusions

Experimental results obtained from SEM and AFM studies showed that the deposition process started at some initial priority centres independently distributed on the deposition surface. Each centre has been composed of agglomerated fine nodules. With increasing complexing agent concentration in deposition bath, P content increases, changing the direction of growth of initial priority from vertical to cross type and reduces surface roughness of deposits. Priority cross growth affects the deposition growing centres and gradually changes their morphology from the coniform to the nodular shapes. Coniform shapes form a rough morphology and nodular shapes form a smooth morphology.

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