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## Making the surface of nanocrystalline Ni on an Si substrate ultrasmooth by direct electrodeposition

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Nanocrystalline (50-µm-thick) Ni films with controlled surface morphology at the nanoscale were synthesized by direct-current electrodeposition of Ni on an Si substrate under different electrochemical conditions. A relationship between spatial roughness scaling and mean grain size in electrodeposited Ni was established using X-ray diffraction and atomic force microscopy. Fractal analysis showed a transition from self-affine to ultrasmooth surfaces. A non-destructive method is demonstrated to estimate the grain size distribution of ultrasmooth nanocrystalline Ni surfaces by atomic force microscopy with high-resolution probes. © 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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The electrodeposition of pure Ni films on Si substrate is commonly used in the fabrication of micrometer-scale applications ranging from microelectronics to microelectromechanical systems. A focal point for research on Ni electrodeposits has been to take full advantage of electrocrystallization processes on surfaces to improve mechanical properties by nanocrystalline grain refinement [1-4]. Microscale fabrication, however, involves additional requirements that do not exist for macroscopic applications. Specifically, a submicroscopic surface structure, such as roughness resulting from film growth, can dramatically change the surface properties of Ni films, e.g. magnetic properties, hardness, tribological behavior and corrosion resistance [5-9]. It is therefore critically important to fully characterize and understand the influence of electrodeposition parameters on the surface morphology of nanocrystalline Ni electrodeposits for microscale devices.

The morphology of electrodeposited Ni surfaces varies significantly as a function of electrochemical conditions [10-15]. Morales et al. [12] have found that, as the electrodeposition current density is increased, both

the Ni crystal size and root-mean-squared (rms) roughness of the deposit is decreased with a Watts plating bath. For larger current densities, however, a change of growth mode operates, making the deposit rougher. Pulse-current electrodeposition is also known to cause anomalous surface scaling, which results in smoother films as compared to direct-current (DC) electrodeposition [13]. Kollia et al. [11] have observed that small variations in pulse-reverse current strongly modify the surface morphology and crystalline orientation in additive-free Ni plating baths. Furthermore, it is well established that the addition of leveling and brightening agents produces a surface transition from "rough" to "smooth" due to the inhibition of grain growth in electrodeposited Ni films [10,14,15]. More specifically, brightening additives are preferentially absorbed at grain growth peaks and inhibit further upward growth, forcing the nucleation of new grains with different texture. This new growth occurs in valleys away from absorption peaks, which accounts for the leveling effect. To our knowledge, however, no direct attempts to synthesize nanocrystalline Ni electrodeposits with a supersmooth, flat surface morphology have been reported in the literature.

This letter demonstrates a method to synthesize thick Ni electrodeposits with ultrasmooth surface structure, i.e. less than 2 nm in rms roughness. The aim of this

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work was to investigate the effects of pH and additives on the surface morphology and mean grain size of nanocrystalline Ni films electrodeposited on Si wafers. The bulk and surface structures of the electrodeposited films were characterized using atomic force microscopy (AFM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). We obtained a quantitative assessment of the spatial roughness scaling as a function of mean grain size in nanocrystalline Ni electrodeposits. Roughness analysis by the power spectral density (PSD) method on AFM topographical scans was also conducted to investigate the smoothening mechanisms. Furthermore, using tapping-mode AFM with high-resolution probes [16], we show that the grain size distribution of ultrasmooth nanocrystalline Ni surfaces can be estimated directly without sample polishing or cutting, as opposed to other techniques of characterization such as transmission electron microscopy.

Nanocrystalline Ni films were grown on an Si substrate by DC electrodeposition. The anode material consisted of a 99.9945%-purity Ni foil. The cathode substrate was an n-type, phosphorus-doped Si (100) wafer (resistivity = 4-8  $\Omega$  cm<sup>-2</sup>) polished on one side. A 100-nm-thick thermal SiO<sub>2</sub> layer was grown in a dry furnace for 16 h, followed by thermal evaporation of a 200-nm-thick Cr/Cu bilayer. The wafer was acid-pickled in a 5% H<sub>2</sub>SO<sub>4</sub> solution for 60 s in order to clean and activate the Cu substrate before plating.

The baths consisted of Ni sulfamate (400 g  $l^{-1}$ ), Ni chloride  $(10 \text{ g } \text{l}^{-1})$  and boric acid  $(30 \text{ g } \text{l}^{-1})$ . The initial pH at 50 °C was equal to 3.8. A 2.0 g l<sup>-1</sup> concentration of Ni carbonate, NiCO<sub>3</sub> · 2Ni(OH)<sub>2</sub>, was used to raise the pH value by approximately 0.2. The Ni carbonate was mechanically agitated in the bath for 30 min. At the desired pH, the entire solution was vacuum filtered through a 1.3 µm paper filter to remove any Ni carbonate precipitates. Conversely, amido-sulfamic acid was used to lower the pH if necessary. Electrodeposition was performed at 50 °C under constant current density  $(18 \text{ mA cm}^{-2})$  until the deposit was about 50 µm in thickness. The plating bath was stirred at constant rate during this process. During electrodeposition, the separation of hydrogen ions from water leads to the formation of hydrogen gas bubbles on the substrate surface, which could increase surface roughness and pitting if Ni is deposited around the bubbles. Therefore, we added

 $2 \text{ ml } l^{-1}$  dipolar surfactant (NP-M2 anti-pitting agent) to decrease the surface tension of the solution and release this gas from the substrate. We studied three types of electrolyte, referred to as baths A, B and C in the following, containing different brightening additives. Bath A was additive-free. To plating bath B, we added  $1.0 \text{ g} \text{ l}^{-1}$  of saccharin. We adjusted the pH value when saccharin was added to the bath, while maintaining the solution temperature at 50 °C to prevent saccharin from precipitating out. 2-Butyne-1,4-diol  $(0.005 \text{ g} \text{ l}^{-1})$ and  $1.0 \text{ g} \text{ l}^{-1}$  of saccharin were added to plating bath C. 2-Butyne-1.4-diol is not co-deposited with Ni and therefore did not require more additions during plating. The pH conditions investigated in this study were 3.8-4.8, 3.0-4.2 and 2.2-4.5 for baths A, B and C, respectively. The samples were thoroughly rinsed in distilled water after plating.

XRD measurements were carried out using Cu  $K_{\alpha}$ radiation ( $\lambda = 1.542$ ) from a sealed tube operated at 40 kV and 35 mA. Diffractograms were recorded using a Rigaku DMax goniometer for diffraction angles  $(2\theta)$ between 40 and 80° at intervals of 0.05° while scanning in  $\theta/2\theta$  mode at a rate of  $0.22^{\circ}$  min<sup>-1</sup>. The mean grain size of the deposits was determined by the Scherrer formula using the full-width half-maxima of the peak broadening to the (111) and (200) XRD reflections. Furthermore, contact-mode AFM imaging was performed in air using standard Si cantilevers (Mikromasch CSC17; tip radius  $\leq 10$  nm; force constant  $\sim 0.15$  N m<sup>-1</sup>) to monitor the smoothening process quantitatively. The scan rate was 1 Hz, with a resolution of 400 lines per scan. We determined the rms roughness  $\xi$  of the electrodeposited surfaces using [12]:

$$\xi = \sqrt{\frac{1}{N} \sum_{n=1}^{n=N} (h_n - \langle h \rangle)^2}$$
(1)

where N is the number of points on the surface,  $h_n$  is the deposit height at point n and  $\langle h \rangle$  is the average height of the sample formed by N points. Three  $1 \times 1 \,\mu\text{m}^2$  AFM scans performed at different locations on the specimen surface were used to determine the average  $\xi$  for each electrodeposit. We also examined how the roughness varied with both height and lateral length scales through PSD analysis [17,18]. The PSD measures, i.e. the



**Figure 1.** Nanocrystalline Ni electrodeposits on an Si (100) wafer obtained from different electrolytes (baths A, B and C) at the same pH ( $\sim$ 3.8). SEM images of (a) a polished cross-section and (b–d) the surface morphology of electrodeposits; (e) corresponding XRD profiles.

squared magnitude of the fast Fourier transform of height profiles, were obtained from  $5 \times 5 \ \mu\text{m}^2$  AFM topographical images. An ensemble average PSD was performed for the surface profile data by calculating the one-dimensional PSD of each profile as a function of the spatial frequency, and the resulting graph averaged over all AFM scan lines to obtain a noise-free curve [17]. For self-affine fractal surfaces and high frequencies, the PSD spectrum displays a power-law scaling behavior expressed by [18]:

$$\langle PSD \rangle \propto f^{-\gamma},$$
 (2)

where f is the spatial frequency and  $\gamma$  is related to the surface fractal dimension by  $D = (8 - \gamma)/2$ .

The electrodeposited Ni films were found to be 45-55 µm in thickness, as shown on the SEM image of a polished cross-section in Figure 1a. SEM images of the surface morphology of electroplated samples obtained at the same pH ( $\sim$ 3.8) with different electrolytes are presented in Figure 1b-d. This figure shows qualitatively that the addition of saccharin and 2-butyne-1,4-diol caused significant surface smoothening, particularly in samples from bath C, where no roughness was visible by SEM (Fig. 1d). Figure 1e presents the effect of plating bath on the XRD plots. The additive-free plating bath A resulted in Ni films with a strong texture in the (200) plane. Samples prepared from bath B exhibited an increased (111) texture and a more moderate (200) texture, which is characteristic of Ni electrodeposition with saccharin [1]. Bath C produced films with a strong (111) texture only. Figure 1e also shows notable peak broadening when saccharin and 2-butyne-1,4-diol are added, suggesting significant grain refinement as discussed below.

The mean  $\xi$  value obtained from different electrolyte and pH conditions is represented in Figure 2 as a function of the mean grain size measured via XRD. This figure confirms more quantitatively that the rms roughness of electrodeposited Ni decreased by more than an order of magnitude by the addition of both saccharin and 2butyne-1,4-diol. Figure 2 also shows that the surface roughness of the deposits was correlated to the mean grain size. For instance, in the  $1 \times 1 \,\mu\text{m}^2$  AFM topographical scans of samples obtained with different plating baths, the rms roughness of the deposits was found to be  $28.7 \pm 6.8$  nm (Fig. 2a),  $4.2 \pm 1.3$  nm (Fig. 2b) and  $1.7 \pm 0.2$  nm (Fig. 2c), and the mean grain size was 32.5, 21.4 and 17.9 nm, respectively. While the pH of the solution appeared to have a small influence on the roughness of the deposits, no clear correlation could be established between these two parameters. This observation supports the idea that the smoothening process was dominated by the addition of 2-butyne-1,4-diol, because this additive is known to play an inhibiting role on the adsorption of hydrogen on electrodeposited Ni surfaces [14,15]. Minimization of hydrogen adsorption was also confirmed by the substantial decrease of the (200) texture observed by XRD on samples from bath C [14]. Furthermore, it is possible to conclude from Figure 2c that smooth nanocrystalline Ni electrodeposits with an rms roughness of less than 2 nm can be fabricated at the micrometer scale by DC electrodeposition in a specific electrochemical environment (i.e. using bath C at pH 2.9).

Figure 3 presents the averaged PSD curves of the specimens featured in Figure 2a–c. This figure shows a decrease in the PSD magnitude when saccharin and 2-butyne-1,4-diol are added, which demonstrates a decrease in rms roughness consistent with the data presented above. Furthermore, the PSD curves for the surface morphology of Ni electrodeposits obtained from additive-free bath A (Fig. 3a) and bath B (Fig. 3b) exhibit clear power-law dependence, as in Eq. (2), with  $\gamma = 3$  for a spatial frequency band between 1 and 10 µm<sup>-1</sup>. This result indicates that the corresponding



**Figure 3.** Averaged power spectral density of the surface roughness of  $5 \times 5 \,\mu\text{m}^2$  AFM topographical images in electrodeposited nanocrystalline Ni from (a) additive-free bath A, with 32.5 nm grain size; (b) bath B, with 21.4 nm grain size; and (c) bath C, with 17.9 nm grain size.



Figure 2. Evolution of rms surface roughness from  $1 \times 1 \mu m^2$  AFM topographical images as a function of mean grain size measured by XRD in electrodeposited nanocrystalline Ni on Si substrate.

electrodeposited surfaces were self-affine, with surface fractal dimension D = 2.5. In contrast, the PSD curve of samples obtained from bath C (Fig. 3c) presents a weak power-law fit with an increased slope close to  $\gamma = 4$  and D = 2. This value of the fractal dimension implies that the electrodeposited Ni surface has no fractal structure and is an idealized, flat surface. The fractal analysis therefore shows that a transition from self-affine surfaces to ultrasmooth, flat surfaces occurred during the smoothening process, along with the decrease in grain size.

We further investigated how ultrasmoothening effects could be exploited in AFM imaging with high-resolution probes to estimate the distribution of grain size on the surface of electrodeposited nanocrystalline Ni. High-resolution AFM probes are standard Si cantilevers with a diamond-like carbon spike grown from the tip, as represented in Figure 4a [16]. Standard AFM probes are typically unable to resolve grains less than 40 nm in diameter due to the large tip radius ( $\sim 10$  nm), while the extra tip of high-resolution AFM probes has a radius of curvature of less than 1 nm, capable of resolving smaller features. Here, we used non-contact high-resolution AFM probes (Mikromasch Hi'Res-DP14; force constant  $\sim 5 \text{ N m}^{-1}$ ; resonant frequency  $\sim 160 \text{ kHz}$ ) to perform low-force, tapping-mode AFM on the surface of the ultrasmooth nanocrystalline Ni electrodeposits. The scan rate was kept small (0.5 Hz) to reduce tip damage. In Figure 4b and d are shown  $400 \times 400 \text{ nm}^2 \text{ AFM}$ topography and phase-mode images, respectively, of the ultrasmooth sample presented in Figure 2c. The contrast on these images must be related to only the grain struc-



Figure 4. High-resolution AFM imaging of nanocrystalline Ni electrodeposit with rms roughness <2 nm. (a) Schematic of tapping-mode AFM with high-resolution probe. (b)  $400 \times 400 \text{ nm}^2$  surface topography image. (c) Grain size distribution obtained from the watershed segmentation method on the phase-mode image shown in (d) with superimposed grain boundary network (in colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ture because no surface roughness is present at this scale. The phase-mode AFM image shown in Figure 4d was treated by watershed segmentation method [19] to estimate the grain size distribution and identify the grain boundary network, as shown in Figure 4c and d, respectively. Figure 4c shows that the grain size distribution obtained from this method is in good agreement with the mean grain size determined from XRD measurements, i.e. 17.9 nm for this particular sample.

In summary, the effects of pH and additives on DC electrodeposition and surface morphology of nanocrystalline Ni on Si substrate have been investigated by AFM and XRD. We found that the surface roughness of nanocrystalline Ni electrodeposits decreased with the grain size due to the synergistic effect of the addition of saccharin and 2-butyne-1,4-diol. A change in surface morphology from self-affine to ultrasmooth and flat was shown for a specific electrochemical environment. Ultrasmoothening effects open up new possibilities for improving the characterization and properties of surfaces in electrodeposited nanocrystalline Ni used for microscale devices.

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