

# Tribological, mechanical and electrochemical properties of nanocrystalline copper deposits produced by pulse electrodeposition

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## Abstract

Nanocrystalline metals and alloys with grain sizes smaller than 100 nm have attracted extensive interest due to their improved mechanical, physical and chemical properties. Although electrodeposition has been one of the methods for synthesizing nanocrystalline materials, properties of nanocrystalline electrodeposits are less evaluated, especially for tribological applications or potential applications in nanoscale devices such as MEMS and NEMS. In this work, nanocrystalline and microcrystalline copper deposits were produced by pulse and direct current electrodeposition processes respectively. Effects of deposition parameters, such as the peak density, frequency, current-on time and current-off time of the pulse current (PC), on the grain size were investigated for the purpose of process optimization. The grain size of nanocrystalline coatings was determined using x-ray diffraction and atomic force microscopy (AFM). Mechanical and tribological properties of the deposits were investigated using nanoindentation, nanoscratch and microscratch techniques. It was demonstrated that the nanocrystalline film was markedly superior to regularly grained film made by direct current (DC) plating; the nanocrystalline deposit shows higher hardness, lower friction coefficient and lower wear rate. The surface electron stability and chemical reactivity of the deposits were also evaluated by measuring their electron work function (EWF). Results indicate that the nanocrystalline surface is more electrochemically stable than the DC-plated one. This increased stability result is attributed to the formation of a stronger and more adherent passive film on the nanocrystalline copper, confirmed by potentiodynamic polarization and electrical contact resistance measurements.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Nanocrystalline metals and alloys, typically with their average grain size smaller than 100 nm, have attracted great interest

in recent years. A number of techniques have been developed to synthesize nanoparticles, such as severe plastic deformation [1], chemical vapour deposition, metal alloying, inert gas condensation [2], electrodeposition [3, 4] etc. Compared to many other methods, electrodeposition is an inexpensive process and offers a simple and variable alternative

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to these complicated and expensive high-temperature or high-vacuum deposition processes. Pulse current electrodeposition, in which current is imposed in a periodic manner with a rectangular waveform, is a powerful means for controlling the electrocrystallization process and producing deposits with unique structure and properties. Many nanocrystalline metals, alloys and composites have been produced by pulse electrodeposition successfully [3]. Some have advanced rapidly to industrial and/or commercial applications, such as production of copper foil for printed circuit boards [3], heat exchanger repair technology [5], production of water resistant coatings [4], electrodes for the catalysis of oxidation and evolution reaction [5] etc.

Compared with direct current plating, pulse current electrodeposition can yield ultra-fine-grained structures and a more homogeneous surface appearance of deposits with improved properties, such as the ductility and hardness [6–10]. More diversified microstructures can be developed, since in PC deposition one can control the microstructure and composition of deposited metals or alloys more effectively by varying the pulse frequency ( $f$ ), the pulse length—current-on time ( $t_{\text{on}}$ ), the time between two pulses—current-off time ( $t_{\text{off}}$ ), the peak current density ( $I_p$ ), the average current density ( $I_a$ ) and the duty cycle ( $\theta$ ). Therein,

$$I_a = \frac{I_p t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}}, \quad f = \frac{1}{t_{\text{on}} + t_{\text{off}}}, \quad \theta = \frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}}. \quad (1)$$

Pulse electrodeposition permits electrolysis with a high current density during a short period of time ( $\mu\text{s}$  ms). The deposition of nanostructured coatings by pulse electrodeposition depends on two fundamental processes, nucleation and growth of grains [10]. During the deposition, these two processes are in competition with each other and are influenced by many factors. Evidently, we are prone to get ultra-fine-grained deposits when the deposited ions are discharged to form new nuclei rather than incorporated into existing crystals. Therefore, factors that usually cause a high nucleation rate and slow grain growth are responsible for the formation of nanograined deposits.

Although PC electrodeposition is one of the effective methods to produce nanocrystalline materials, the properties of such fabricated nanocrystalline electrodeposits are less investigated in the literature compared to those made by CVP or the condensation method [3]. Especially, the corrosion resistance and tribological properties of nanocrystalline electrodeposits need to be fully evaluated, since this is of great importance to a wide range of potential industrial applications of the nanodeposits. Previously reported studies are not always consistent. It was demonstrated that the coefficient of friction for nanocrystalline Ni produced by PC plating was almost half that of polycrystalline Ni [11]. The incorporation of nanodiamond particles into the microcrystalline Ni matrix significantly increased the overall mechanical and tribological properties, but the nanocrystalline Ni matrix composites exhibited much poorer anti-wear performance than pure nanocrystalline Ni under dry sliding wear conditions [12]. Nanocrystalline Zn coatings exhibited improved corrosion resistance compared to electrogalvanized steel in 0.5 N NaOH solution due to a more protective passive film formed [13]. The passive current density of nanocrystalline Ni was found to

**Table 1.** Electrolytes and deposition parameters for Cu deposition.

Constituents	PC-plating bath	DC-plating bath
CuSO <sub>4</sub> ·5H <sub>2</sub> O	0.15 M	0.6 M
H <sub>2</sub> SO <sub>4</sub>	0.184 M	0.46 M
Thiourea	0.05 gl <sup>-1</sup>	0.05 gl <sup>-1</sup>
Deposition parameters	$I_p = 1 \text{ A cm}^{-2}$ $t_{\text{on}} = 0.1 \text{ ms}$ $t_{\text{off}} = 9.9 \text{ ms}$ $f = 100 \text{ Hz}$ $I_a = 10 \text{ mA cm}^{-2}$	$I = 10 \text{ mA cm}^{-2}$

be higher in acidic, alkaline and neutral solutions than that of polycrystalline Ni, etc [14].

The objective of the present study is to investigate the tribological, electrochemical and mechanical properties of nanocrystalline Cu deposits produced by PC electrodeposition in comparison with microcrystalline ones produced by DC electrodeposition. Another task is to correlate changes in the properties to the grain size. With the rapid development of nanotechnology, nanotribology becomes more and more important to devices on the nanoscale such as MEMS, NEMS and magnetic storage peripherals [15, 16]. Copper was chosen as a sample material in view of its applications as an interconnect material in microelectronic devices as well as its wide applications in the integrated circuit industry. Copper deposits have also found applications in nickel and chromium plating as an undercoat [17]. However, research in tribological and electrochemical properties of nanocrystalline Cu deposits is still scarce and, in particular, few studies have addressed the tribological issue.

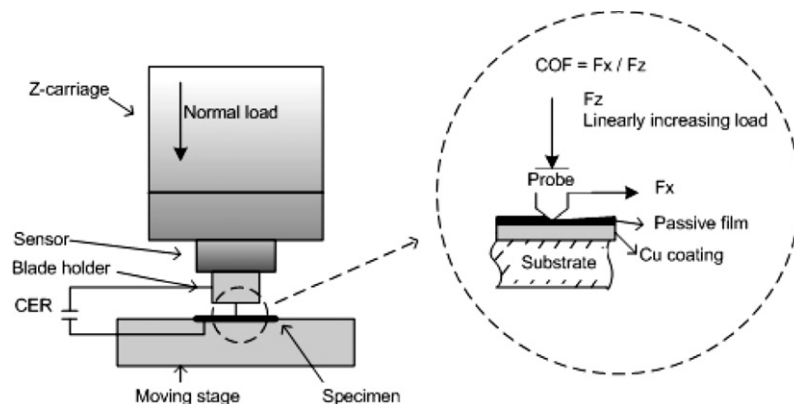
## 2. Experimental procedure

### 2.1. Specimen preparation

Nanocrystalline and microcrystalline copper deposits were produced respectively by pulse current and direct current electrodeposition processes in copper sulfate electrolytes with thiourea as additive. Chemical compositions of two types of electrolyte and their corresponding deposition parameters are listed in table 1. Brass was used as the substrate, which was polished followed by weak and strong pickling in 3% and 25% H<sub>2</sub>SO<sub>4</sub> solutions, respectively. Pickling was carried out in order to activate the substrate and improve the adhesion of deposits. The counter-electrode was pure copper, which helped to maintain the copper ion concentration in electrolyte. After electrodeposition, the copper deposits were rinsed in de-ionized water and dried immediately. The deposits were slightly polished with 0.05  $\mu\text{m}$  alumina powder and lightly etched using dilute FeCl<sub>3</sub> + HCl solution before testing their properties. The thickness of the deposits was about 15  $\mu\text{m}$ , estimated based on the weight gain of the brass electrode as well as microscopic observation of cross-section.

### 2.2. Morphology characterization and mechanical property evaluation

The grain size of the nanocrystalline deposits was determined using both the x-ray diffraction peak broadening analysis and atomic force microscopic (AFM, provided by Digital



**Figure 1.** Schematic diagram of the scratch test for the passive films on Cu coatings with *in situ* monitoring of the contact electrical resistance (CER).

Instruments, Santa Barbara, CA, USA) image observation. X-ray diffraction analysis was carried out using a Rigaku Geigerflex Power Diffractometer with a Co tube and a graphite monochromator. The wavelength of Co  $K\alpha$  radiation is 0.178 897 nm. Each diffraction peak profile was obtained at a slow scan rate of  $0.002 \text{ s}^{-1}$ . The surface morphology of deposits was characterized by the AFM technique in both friction and contact modes of scanning. A  $200 \mu\text{m}$  long narrow silicon nitride probe with a spring constant of  $0.06 \text{ N m}^{-1}$  was used. The probe consisted of a cantilever with an ultra-sharp tip at the end. The height of the tip was about  $10 \mu\text{m}$ .

Mechanical properties of the deposits were characterized using a Triboscope (made by Hysitron, Minneapolis, MN, USA), a combination of nanomechanical probe and atomic force microscope. The probe was a three-sided pyramidal Berkovich indenter made of diamond. The angle between two faces of the tip is  $142.3^\circ$ . Force–displacement curves of indentation were recorded during the test. Indentation loads of 50 and  $100 \mu\text{N}$  were used. Hardness and elastic behaviour of the deposits were evaluated from the force–displacement curves and the results presented in this article are values averaged over more than ten indents.

### 2.3. Electrochemical behaviour and surface stability analysis

Dynamic polarization measurement was carried out using a commercial electrochemical system (made by Gamry Instruments Inc, Warminster, PA, USA) by sweeping the potential at a scan rate of  $5 \text{ mV s}^{-1}$  from  $-300$  to  $1000 \text{ mV}$  about the corrosion potential in a  $0.1 \text{ M NaOH}$  solution. The anodic Tafel slope ( $\beta_a$ ) and cathodic Tafel slope ( $\beta_c$ ) were determined by scanning the potential at  $0.5 \text{ mV s}^{-1}$  in the range of  $\pm 100 \text{ mV}$  about the corrosion potential. Linear polarization resistance was determined by performing polarization at a scanning rate of  $0.1 \text{ mV s}^{-1}$  in the range of  $\pm 5 \text{ mV}$  about the corrosion potential. Before the electrochemical tests, coatings were mounted using epoxy with a surface area of  $100 \text{ mm}^2$  exposed to the corrosive medium and then stabilized in the system for 30 min. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate was used as the counter-electrode. All electrochemical tests were performed at room temperature. The corrosion potential,

passive current density and corrosion rate were determined from the polarization curves.

The electrochemical stability of coating surfaces was evaluated using a scanning Kelvin probe (SKP, provided by KP Technology Ltd, Wick, UK) by measuring their electron work function (EWF) under the ambient condition. The system could control the spacing between the probe tip and the tested surface within  $40 \text{ nm}$  with high resolution ( $< 50 \mu\text{eV}$ ). A gold tip of  $1 \text{ mm}$  in diameter was used to scan the surface with an area of  $2 \times 2 \text{ mm}^2$  covering  $10 \times 10$  measurement points. The EWF was determined by an average value over the scan area. The oscillation frequency of the SKP tip was  $173 \text{ Hz}$ .

The failure resistance of the passive films formed on the deposits was evaluated by scratch tests using a universal microtribometer (UMT, provided by CETR, Mountain View, CA, USA). Before tests, the passive films on the PC- and DC-plated deposits were formed by immersion in  $0.1 \text{ M NaOH}$  under an imposed potential of  $0.1 \text{ V}$  (versus SCE) for 1 min at room temperature. Figure 1 is a schematic illustration of the scratch test performed on the passive film on a Cu coating surface. During the scratch test, the surface was scratched under a normal load, which was increased linearly from 0 to  $10 \text{ g}$ . The scratch probe was made of tungsten carbide. The information of the probe geometry can be found in [18]. During scratching, the tip scratched the surface under the applied load at a velocity of  $0.05 \text{ mm s}^{-1}$ . At the same time, changes in the contact electrical resistance (CER) between the tip and specimen surface with respect to the load were recorded. When the passive film failed under a critical load, the CER value dropped steeply. The critical load is therefore a measure of the resistance of a passive film to failure. Critical loads of different deposits were obtained by averaging more than 5 measurements.

### 2.4. Tribological property evaluation

Friction coefficients of the PC- or DC-plated deposits under relatively higher loads were measured using a sharp conical tip ( $30^\circ$  cone angle) and a ball tip (diameter  $4 \text{ mm}$ ) made of stainless steel respectively attached to the universal microtribometer. Sliding tests were carried out under a series of normal constant loads at a velocity of  $0.05 \text{ mm s}^{-1}$  over