

## KPAN008: Application – Nanotechnology

*“Tribological, mechanical and electrochemical properties of nanocrystalline copper deposits produced by pulse electrodeposition” -*

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### Keywords

Work Function, WF, Kelvin Probe, Nanocrystalline, Tribology, Grain Boundary, Pulse Current

### 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 synthesising 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 optimisation. 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 polarisation and electrical contact resistance measurements.



Figure 1. KP Technology SKP5050 Scanning Kelvin Probe System

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### Research Area

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 synthesise nanoparticles, such as severe plastic deformation, chemical vapour deposition, metal alloying, inert gas condensation, electrodeposition etc.

Compared to many other methods, electrodeposition is an inexpensive process and offers a simple and variable alternative 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 electrocrystallisation process and producing deposits with unique structure and properties. Many nanocrystalline metals, alloys and composites have been produced by pulse electrodeposition successfully. Some have advanced rapidly to industrial and/or commercial applications, such as production of copper foil for printed circuit boards, heat exchanger repair technology, production of water resistant coatings, electrodes for the catalysis of oxidation and evolution reaction 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. 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 ( $t_{on}$ ), the time between two pulses—current-off time ( $t_{off}$ ), the peak current density ( $I_p$ ), the average current density ( $I_a$ ) and the duty cycle ( $\theta$ ). Therein,

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

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. 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.

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. 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. However, research in tribological and electrochemical properties of nanocrystalline Cu deposits is still scarce and, in particular, few studies have addressed the tribological issue.

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### Use of Kelvin Probe

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 nm with high resolution ( $<50 \mu\text{eV}$ ). A gold tip of 1 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 Hz.

Specimen	mc-Cu ( $2 \mu\text{m}$ )	nc-Cu (56 nm)
EWF (eV)	$4.12 \pm 0.04$	$4.30 \pm 0.04$
Critical load corresponding to CER drop (g)	$2.2 \pm 0.3$	$3.3 \pm 0.4$
Corrosion potential (mV)	$-230 \pm 4$	$-248 \pm 5$
Polarization resistance ( $\Omega \text{ cm}^2$ )	$2238 \pm 42$	$4780 \pm 36$
Tafel slope $\beta_a$ (mV/decade)	$51.5 \pm 5.6$	$44.6 \pm 4.8$
Tafel slope $\beta_c$ (mV/decade)	$393.7 \pm 2.5$	$398.9 \pm 7.8$
Corrosion current density ( $\mu\text{A cm}^{-2}$ )	8.8	3.6

Table 1. EWF, critical load at the drop in CER, and corrosion rate of different specimen surfaces

The chemical stability of Cu deposits was investigated by measuring their EWF. As a sensitive characteristic of a solid surface, the work function reflects the inertness of a surface to environmental influence or its resistance to electrochemical attack. Generally, the lower the EWF, the more active are the surface electrons. Average EWF values of nanocrystalline (grain size  $d = 56 \text{ nm}$ ) and microcrystalline ( $d = 2 \mu\text{m}$ ) Cu deposits and their typical EWF diagram are shown in table 1 and figure 2, respectively. It was demonstrated that the nanocrystalline

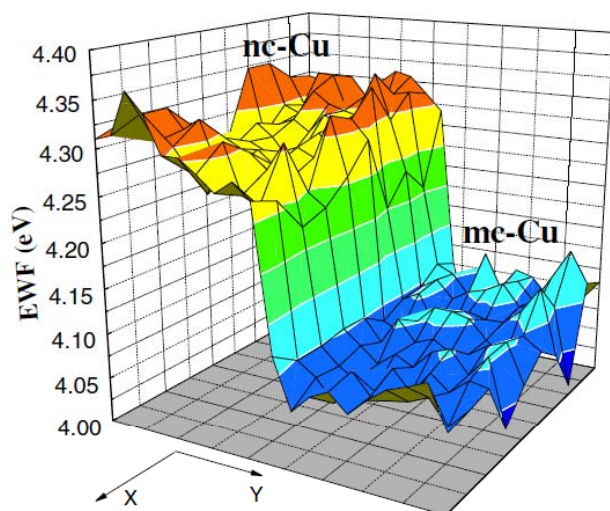


Figure 2. EWF of nanocrystalline (56 nm) and microcrystalline ( $2 \mu\text{m}$ ) Cu deposits. (X and Y are co-ordinate axes for the scanned area.)

surface had higher EWF and thus was more electrochemically stable than the microcrystalline one. This may be explained when the formation of a passive film on the deposit is taken into account. The nanocrystalline copper coatings have higher grain boundary density than microcrystalline ones, which should render electrons more active and thus accelerate the formation of a protective passive film. The higher EWF of the nanocrystalline deposit is attributed to its high density of grain boundaries, which promote the formation of an oxide film ( $\text{Cu}_2\text{O}$  or  $\text{Cu}(\text{OH})_2$ ) on the deposit during etching. The

formation of passive films on the corroded surface is controlled by diffusion. It is reported that nanocrystalline materials, which have higher density of grain boundaries than microcrystalline ones, exhibit anomalously enhanced diffusion properties owing to rapid mass transport along grain boundaries, where diffusion is usually much faster than in crystals. A more protective passive film could lead to a decrease in EWF or an increase in the surface electron chemical stability



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### Conclusion

Nanocrystalline and microcrystalline copper deposits were produced by PC and DC electrodeposition processes, respectively. The grain size of the nanocrystalline deposit was about 56 nm determined by XRD and AFM. Changing the electrodeposition parameters, e.g.,  $t_{on}$ ,  $t_{off}$  and  $I_p$ , is an effective way to control the grain size and corresponding properties of the deposit. Mechanical and tribological properties of the nanocrystalline copper film are markedly superior to those of the DC-plated film. The nanocrystalline surface with higher EWF value was more electrochemically stable than the DC plated one. The nanocrystalline deposit could form a more protective and adherent passive film than the microcrystalline one.

### Reference

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