

Electrochemical Characterization of Copper Deposited on Plasma and Thermally Modified Titanium Surfaces

K.S. TENG, J.-L. DELPLANCKE, J. ZHANG, and T.J. O'KEEFE

Thin oxide films were grown at temperatures from 373 to 1073 K in plasma and in air on commercially pure titanium substrates. It was determined that the color, thickness, composition, phase, and polarization behavior in a copper electrolyte varied with operating conditions: temperature, oxygen partial pressure, and plasma composition. High-temperature and high oxygen partial pressure plasma produced a thick oxide film. The surface film structure transformed from TiO_2 (anatase) to TiO_2 (rutile) at a temperature of 600 °C. A lower oxide of the form $\text{Ti}_n\text{O}_{2n-1}$, such as Ti_2O_3 (which may be porous) or possibly Ti_3O_5 , was formed on a thermally treated sample (400 °C, 80 mtorr O_2 , 3 hours). This sample exhibited the lowest potential for copper nucleation and gave a very uniform, smooth, and hole-free copper foil.

I. INTRODUCTION

Titanium has been used successfully as a cathode substrate in a variety of electrochemical operations.^[1] One of the main reasons titanium is adopted is the excellent corrosion resistance provided by the oxide film formed on its surface. Most applications employ the titanium with a naturally formed oxide. The primary objective of this research was to determine if thermally produced films would modify the electrochemical behavior of the surface.

A variety of methods have been used to form titanium dioxide thin films, including anodization (1 M pure sulfuric acid),^[2] furnace oxidation,^[3] evaporation or sputtering of TiO_2 ,^[4,5] metallo-organic chemical vapor deposition,^[6] and chemical vapor deposition.^[7] Among these, furnace oxidation is the least complicated in generating reproducible oxide thin films. Although the high-temperature properties of titanium have been extensively evaluated, few studies have been made on the effect of the oxide phase on electrocrystallization. This is particularly true for research conducted on generating films below 800 °C, as the surface titanium dioxide films are often too thin to be characterized using X-ray diffraction (XRD) techniques.

Over the past decade, a variety of applications relating to the area of surface coating using plasma treatment techniques have been identified. For example, high dielectric constant titanium dioxide thin films have been formed on silicon substrates by plasma oxidation of titanium.^[8] Plasma oxidation of silicon has been used in integrated circuits to form high quality insulating oxide layers. Scheider *et al.*^[9] reported that aluminum samples oxidized in plasma showed significant increases in oxygen diffusion. Plasma-treated

Cu-Al alloy also enhanced the reaction rate and caused selective oxidation. Thus, a thermally or plasma-modified surface has been shown to cause a variety of changes in behavior of the metal substrate.

In this study, the oxide films were grown on titanium by plasma and thermal oxidation at various temperatures (ambient temperature to 800 °C) and oxygen partial pressures (air or 80 mtorr O_2). Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Auger electron spectroscopy (AES), and XRD were used to characterize the thin films. Particular attention was given to the electrochemical behavior of the various oxides with respect to the polarization and electrocrystallization of copper on the various surfaces.

II. EXPERIMENTAL

A. Plasma and Thermal Treatments

The apparatus used for the plasma oxidation treatment has been described in detail previously.^[10] The reactor consisted of a glass chamber, a resistance heating plate to control substrate temperature, 17-turn, 1/4-in. copper coil, and 120 W RF input power (13.56 MHz). Before introducing oxygen, the reactor was evacuated to 1 mtorr and a flow rate of 0.5 sccm was used during the 3-hour experiments. The system pressure was maintained at 80 mtorr by adjusting the main valve of the reactor.

Thermal oxidation treatments were also conducted in the same reactor but without the plasma. The temperature was varied from 200 °C to 800 °C in air or with a 80 mtorr oxygen partial pressure, the latter maintained by introducing pure oxygen at a flow rate of 0.5 sccm. The reactor temperature was calibrated by comparing the readings of the thermocouple, which was embedded in a graphite block, with the melting point of pure metals in the same range, namely, tin and lead.

B. XRD, AES, SEM, and TEM Examination

A General Electric XRD-5 diffractometer with $\text{Cu } K_\alpha$ radiation was employed for the phase and orientation determinations. Oxygen composition profiles of the titanium substrates were made by using a Physical Electronics

K.S. TENG, formerly graduate student with the Materials Research Center at the University of Missouri-Rolla, is now Integration Engineer with Winbond Electronics Corp., Taipei, Taiwan. J.-L. DELPLANCKE, Lecturer, Department of Metallurgie-Electrochimie, is with the Universite Libre de Bruxelles, B-1050 Bruxelles, Belgium. J. ZHANG, formerly graduate student with the Materials Research Center at the University of Missouri-Rolla, is currently with Caterpillar, Peoria, IL 61656. T.J. O'KEEFE, Professor, is with Department of Metallurgical Engineering and the Materials Research Center, University of Missouri-Rolla, Rolla, MO 65409-1170.

Manuscript submitted June 27, 1995.

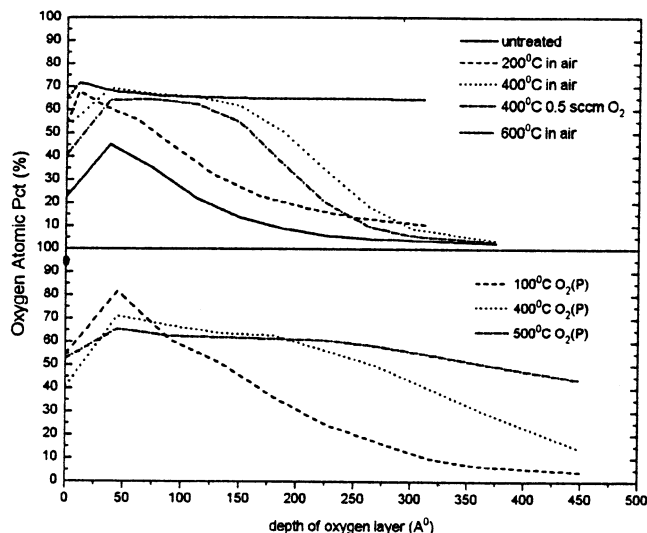


Fig. 1—AES depth profiles for oxygen in titanium samples treated under different oxidation conditions for 3 h.

Model 545 AES operated at an initial pressure below 5×10^{-9} torr. The AES sputter depth profiles were produced by Ar-ion bombardment at a voltage of 2 kV with a pressure of 5×10^{-5} torr and a current intensity of 10 mA. The sputter rate was estimated to be 45 Å/min by calibration with a 1000 Å thick Ta₂O₅ film.

A JEOL* T330A scanning electron microscope was used

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

to examine the morphology of the oxide films and of the copper deposited on the various titanium substrates. The structure of the titanium oxide films was determined at high magnification with a PHILIPS** CM20 ultrathin scanning

**PHILIPS is a trademark of Philips Electronic Instruments, Mahwah, NJ.

transmission electron microscope (STEM) with an accelerating voltage of 200 kV. The oxide films were stripped from the titanium substrates as described by Nurse and Wormwell.^[11] Transmission high energy electron diffraction (THEED) in the STEM was used for phase determination.

C. Electrochemical Measurements

Electrochemical system

The electrolytic cell was a jacketed glass beaker with a polyethylene foam cell cover, and a three electrode design was used for all measurements. The working electrode was the treated titanium substrates with a platinum mesh used as the counterelectrode. A mercury/mercurous sulfate electrode (Hg/Hg₂SO₄, + 0.656V vs SHE) fitted with a Luggin capillary served as the reference electrode, and all reported potentials were given with respect to this reference. The stock electrolyte was made from certified grade cupric sulfate pentahydrate and reagent sulfuric acid to give a composition of 40 g/L Cu²⁺ and 180 g/L H₂SO₄. The electrolyte was not stirred and was maintained at 40 °C during the deposition tests.

Electrochemical polarization measurements were carried out by means of a EG&G Princeton Applied Research-273 potentiostat. The polarization curve data were recorded and

Table I. The Thickness and Color of Titanium Oxide Films on As-Received Substrates and Substrates Treated by Plasma and Thermal Oxidations

Temperature (°C)	Environment	Oxidation Duration (Hours)	Color	Thickness (Å)
Untreated	—	3	colorless	200
100	oxygen plasma	3	light gold	290
200	air	3	light gold	300
400	oxygen plasma	3	gold	500
400	80 mtorr oxygen	3	gold	320
400	air	3	gold	360
500	oxygen plasma	3	blue	960
600	air	3	blue	>1500
800	air	3	gray	>3000

processed using an IBM PC* with Head Start version 1.1

*IBM PC is a trademark of International Business Machines Corp., Armonk, NY.

software. The potential was scanned from -350 to -700 mV with respect to a Hg/Hg₂SO₄ reference electrode at a rate of 0.5 mV/s.

A constant cathodic current density of 40 mA/cm² for 30 minutes was used to deposit copper onto the thermally or plasma-oxidized titanium substrates. The copper foil was stripped from the titanium substrates for SEM evaluation.

III. RESULTS AND DISCUSSION

A. Oxide Film Color/Thickness

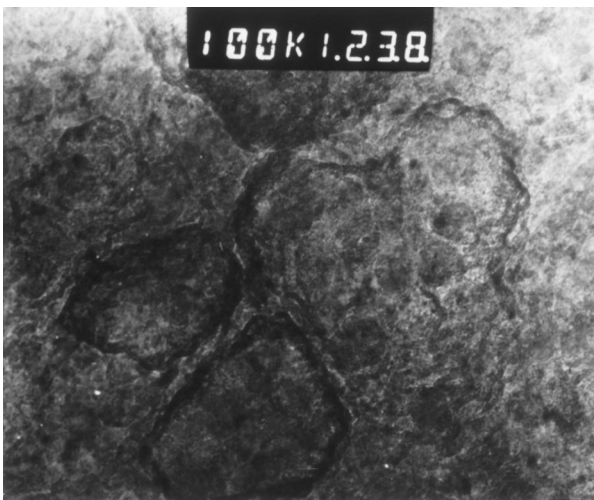
The color of the titanium varied with oxidation temperature, oxygen partial pressure, and time, as expected. According to Fukuzuka *et al.*,^[12] titanium oxide films show various colors due to light interference, depending on their thickness. In this study, as the oxidation temperature increased from 100 °C to 800 °C, the color of the titanium oxide film changed from gold, to blue, and finally to gray.

The thickness of surface oxide film was semiquantitatively determined by AES. The oxide film became thicker when the oxygen partial pressure and oxidation temperature increased. The oxygen plasma-treated titanium showed a deeper penetration of dissolved oxygen and a thicker oxide film than the air oxidized samples, both processed at the same temperature, as seen in Figure 1. For the titanium sample oxidized at low temperature (200 °C), the oxygen composition was relatively high at the outer surface but decreased very rapidly. The titanium samples treated at 300 °C to 500 °C showed an oxygen composition peak near the surface, followed by a broader plateau at about 65 at. pct oxygen, then decreased slowly into the bulk titanium. At temperatures near 800 °C, a fixed oxygen composition of 65 at. pct oxygen was observed from the surface into the bulk, within the measurement range used. A different oxygen distribution was found using 400 °C and 80 mtorr O₂. The initial oxygen peak disappeared, leaving only a plateau with a constant composition of 64 at. pct.

Thermal oxidation at 400 °C in air or 80 mtorr O₂ gave oxides with similar thicknesses. Compared with the thermally treated samples, plasma oxidation significantly increased the depth of oxygen penetration film (Table I). The



(a)



(b)

Fig. 2—STEM surface microcrystals of oxide film formed at (a) 200 °C, O₂(P), 3 h; and (b) 400 °C, O₂(P), 62 h.

Table II. Titanium Oxide Phases Determined by THEED Analyses

Temperature (°C)	Environment	Phase (THEED)
Untreated	—	— (too thin)
200	air	— (too thin)
200	oxygen plasma	TiO ₂ (anatase + brookite)
400	oxygen plasma	TiO ₂ (anatase) + unknown phase
400	80 mtorr oxygen	suboxide phase Ti _n O _{2n-1}
400	air	TiO ₂ (anatase) + unknown phase
600	air	TiO ₂ (anatase + rutile)
800	air	— (too thick)

enhancement of oxidation is not surprising, because the energetic plasma flux increases the oxygen diffusion and species activity, and ion bombardment may cause an increase in the localized surface temperature. Similar phenomena have been reported in ion plating.^[13]

The thickness-color relationship proposed for titanium oxide films was in agreement with the results of the Auger analyses. As the film thickness increased from 500 Å, to

1000 Å, and finally to 3000 Å, the color of the samples changed from gold, to blue, and then to gray (Table I).

B. Phase Analysis

The oxide films produced by thermal and plasma oxidation in 3 hours at temperatures between 200 °C and 600 °C are too thin to be analyzed by XRD or by grazing angle XRD. The phase composition of these oxide films was then only detected by THEED in the electron microscope. The thermal and plasma oxidized samples were more difficult to strip from their substrates than the anodic oxide films.^[14] This is probably due to the absence of surface polishing of the sample prior to oxidation. The films grown at temperatures lower than 400 °C were perfectly uniform and without any measurable crystalline structure. At 400 °C, the same result was obtained for 3 hours oxidation. On the contrary, for 62 hours oxidation, microcrystals were visible, as seen in Figure 2. For higher temperature oxidation, regardless of oxidation duration, the films were crystalline. Due to the small dimensions of the diffracting crystals, the phase determination was often difficult.

For samples oxidized at 400 °C and 600 °C, anatase and a mixture anatase/rutile were detected, respectively. The XRD detected rutile for the samples oxidized at 600 °C and 800 °C. This transition temperature between anatase and rutile was lower than the transition temperature mentioned in the literature for thermal transformation (1100 °C^[15]). For the samples oxidized in the O₂ plasma, similar results were obtained. An absence of structure and of crystallization was observed up to 400 °C and anatase was present at higher temperatures.

For the films grown using an oxygen partial pressure of 80 mtorr at 400 °C, a crystalline film is detected. Due to the small number of peaks detected, an accurate identification of the crystalline phase was not possible, but a suboxide of some type is suspected. The formation of such phases has been observed for rutile TiO_{2-x} in a reducing atmosphere.^[16] In this case, a suboxide phase was formed at 400 °C at 80 mtorr O₂ for 3 hours, indicating that low oxygen partial pressures favor lower oxide formation.

All the phases found using THEED analyses are listed in Table II.

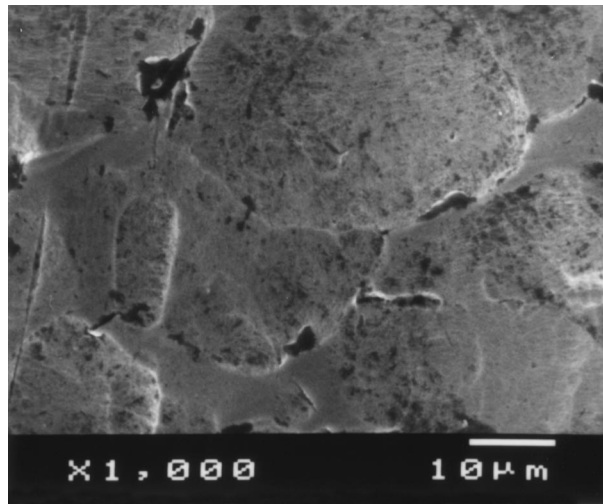
C. Morphology

Compared with the as-received samples, no significant changes were observed for the titanium plasma oxidized at low temperature (<300 °C) and/or low oxygen partial pressure (80 mtorr O₂) (Figure 3). As the oxidation temperature increased to 400 °C or 500 °C, a fine, scalelike structure formed, in a manner similar to that reported in the literature.^[17]

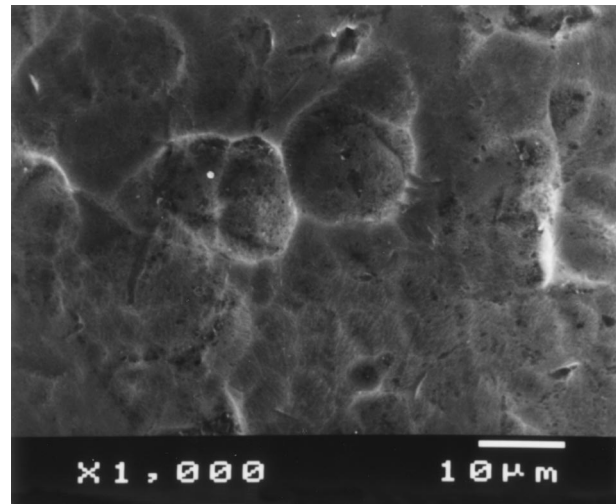
D. Electrochemical Response

The polarization curves generated using an acidic copper-sulfate bath and the plasma-oxidized titanium substrates are shown in Figure 4. The potential for copper nucleation and growth became more negative (polarized) when the oxidation temperature was below 200 °C.

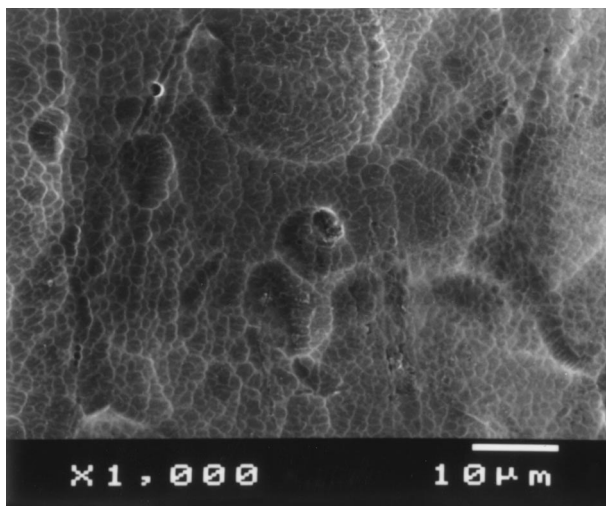
The potential became more positive, indicating that copper nucleation and growth were enhanced, when oxidation



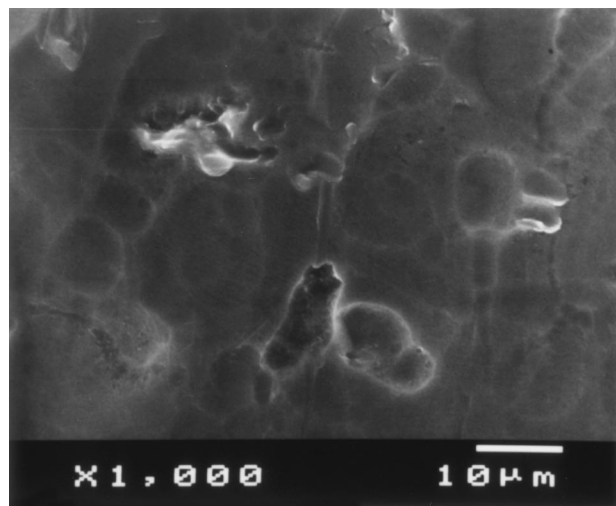
(a)



(b)



(c)



(d)

Fig. 3—SEM surface micrographs of oxide films formed at (a) untreated; (b) 100 °C, O₂(P); (c) 500 °C, O₂(P); and (d) 400 °C, 80 mtorr O₂.

temperatures of 300 °C to 500 °C were used. At an oxidation temperature of 800 °C, no copper was deposited on the titanium electrode, even at relatively high potentials, due to the insulating oxide film on the surface. The results indicate clearly that the surface oxide phase and thickness are determining factors in copper nucleation. In addition, the thickness alone is not the determining factor since some thinner oxide layers are more polarizing than thicker ones formed at higher temperature.

The polarization curves for copper deposition on the titanium substrates treated in different oxygen partial pressures (80 mtorr, O₂ plasma, air) are summarized in Figure 5. Low oxidation temperatures caused polarization, while higher temperatures depolarized the reaction. This was independent of the applied oxygen partial pressure. The strongest depolarizing effect was observed for surfaces oxidized at 400 °C and 80 mtorr O₂. A very substantial decrease in relative overpotential of 120 mV for copper nucleation was measured, compared to the untreated as-received substrate. Also, the polarization curve for copper deposition on the titanium substrate treated in an O₂ plasma was in an intermediate position between the air and 80

mtorr O₂ oxidation-treated substrates. Both the O₂ plasma and 80 mtorr oxidation at 200 °C gave similar increases in polarization.

Considerable research^[18,19] has previously been focused on the kinetics of redox reactions at film covered metal electrodes. From these experiments, a rather consistent behavior was observed. For thin films, electron transfer was dependent on the film thickness. For thick films, the semiconductor nature of the oxide was important. However, it is difficult to quantitatively define the boundary thickness separating thin from thick films for various metals and alloys. For the film formation on titanium substrates by plasma and thermal treatment, a wide range of 200 to 3000 Å film thicknesses was observed (Table I) and thick film behavior should be considered particularly for samples treated at the higher temperatures.

Oxide morphology and phase changes are possible causes for the overpotential changes observed during copper deposition on the titanium substrates. As seen in Figure 2, microcrystals were formed at higher temperatures (>400 °C). The presence of the microcrystals in the oxide layer on the titanium substrates greatly enhanced copper nucle-

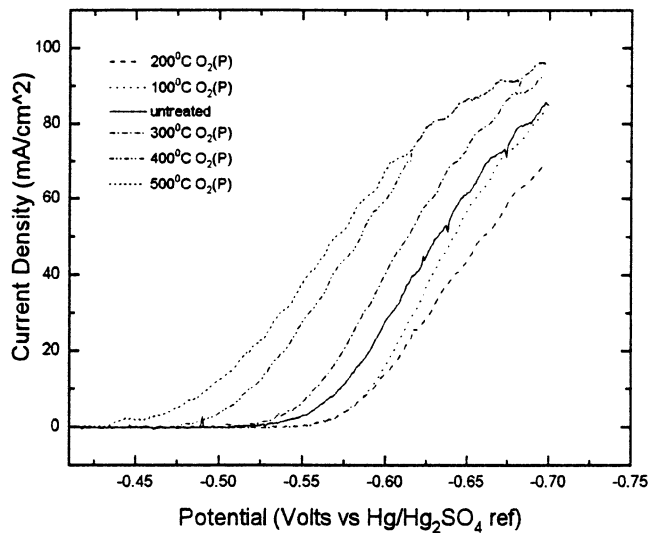


Fig. 4—Polarization curves recorded for 40 g/L Cu^{2+} and 180 g/L H_2SO_4 sulphuric acid electrolyte using as-received titanium substrates and substrates after plasma oxidation at different temperatures.

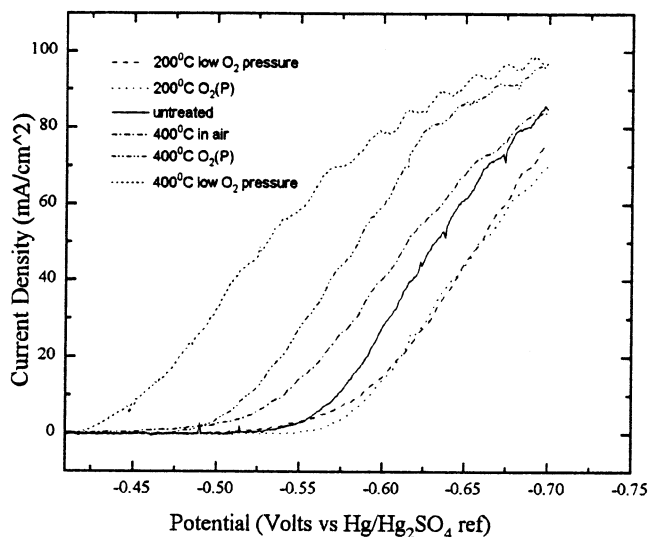


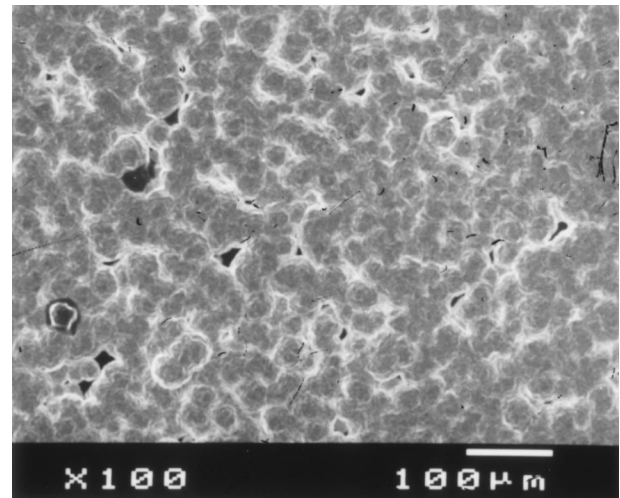
Fig. 5—Polarization curves recorded for 40 g/L Cu^{2+} and 180 g/L H_2SO_4 sulfuric acid electrolyte using as-received titanium substrates and substrates pretreated by different plasma and thermal oxidation.

ation and growth. Either enhanced conductivity or the more favorable surface structure of these areas might create lower energy sites for stable nuclei formation.

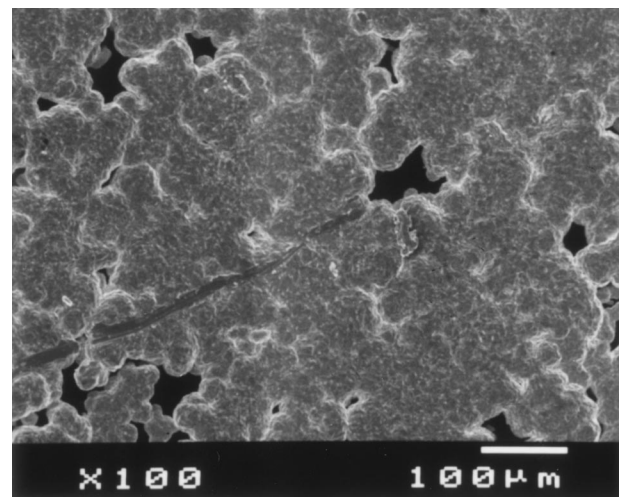
Another possible mechanism could be electrical conductivity, which involved phase changes. This kind of mechanism was proposed by Delplancke and Winand.^[14,20] Some highly conductive clusters were found in anodized titanium films, which contained a small number of highly oriented microcrystals. Such sites could act as preferential conducting channels, allowing copper nucleation to occur more easily at these selected locations.

E. Galvanostatic Deposition

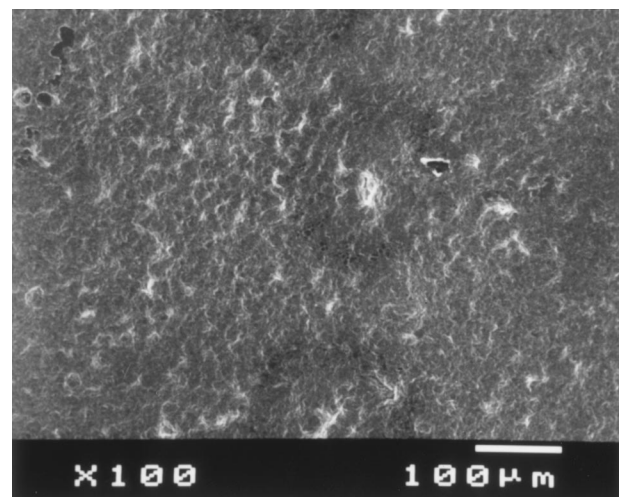
Morphology studies were made using copper deposited at 40 mA/cm² for 30 minutes on the various substrates and are shown in Figure 6. A rather porous, or discontinuous, deposit was made on the titanium substrates treated at 200



(a)



(b)



(c)

Fig. 6—Copper deposited at 40 mA/cm² for 30 min on titanium substrates treated at different conditions: (a) as-received; (b) 200 °C, O_2 (P); and (c) 400 °C, 80 torr O_2 .

°C in an O_2 plasma. The deposit on untreated titanium showed some open areas, but the overall coverage was rea-

sonably good. A very uniform, smooth, and pore-free copper film was formed on the titanium substrate treated at 400 °C in 80 mtorr O₂ partial pressure. The differences noted were in agreement with the polarization curves. A low nucleation overpotential resulted in high quality thin copper films. Now that the importance of surface oxide phase on copper nucleation has been observed, additional research is planned to study the mechanism involved for the different substrates.

IV. CONCLUSIONS

To date, much of the research on improving the electrocrystallization of deposited films has centered on modifications to the electrolyte. The use of additives to enhance metal properties, smoothness, and uniformity has been particularly prevalent. The primary objective of these studies was to gain a qualitative estimate of the magnitude of change that might result from modifying the initial cathode surface. Previous reports^[21,22] revealed that substantial changes could be produced when the titanium substrate was anodized to give different surface phases and morphologies. Thermal and plasma oxidation treatments were chosen for evaluation in this work. The data indicate that rather substantial changes in the polarization behavior of copper deposited from an acid sulfate electrolyte can result.

At low oxidation temperatures, the films were too thin to determine their degree of crystallinity. Copper deposited at 40 mA/cm² for 30 minutes on various substrates was used for the morphology studies and the results are shown in Figure 6.

At higher temperatures, a crystalline TiO₂ structure was detected, which is more conducting and enhances copper deposition by lowering copper nucleation and growth overpotential.

The best results (very dense uniform and hole-free copper deposit) were obtained for films grown under low oxygen partial pressure, which may promote the growth of a suboxide phase of some type whose composition has yet to be confirmed. The overall results were very definitive in establishing the important role that the titanium oxide films have on copper electrocrystallization. Additional research to more clearly identify the specific mechanisms responsible could be valuable in furthering a fundamental understanding of metal deposition processes. Specifically, a better explanation for the actual cause of the enhanced copper nucleation on the various titanium oxide surfaces is needed.

ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by the United States Department of Energy (DE-FG01-91CE15452), NSF-INT 8818746, and Kidd Creek Mines Ltd. (Timmins, On).

REFERENCES

1. A.G. Ives, J.R.B. Gilbert, and J.P.A. Wortley: *Nucleation and Growth of Copper Electrodeposits on Titanium*, 103rd Annual Meeting, AIME, Dallas, TX, 1974.
2. J.-L. Delplancke: Anodisation autocolorée du titane, Travail de Fin d'Études en vue de l'obtention du Grade d'Ingenieur Civil Chimiste, Université Libre de Bruxelles, Bruxelles, 1981.
3. Y. Katsuta, R. Akahane, and K. Yahagi: *J. Appl. Phys.*, 1971, vol. 10, p. 976.
4. W.D. Brown and W.W. Grannemann: *Solid-State Electron.*, 1978, vol. 21, p. 837.
5. M. Takeuchi, T. Itoh, and H. Nagaska: *Thin Solid Films*, 1978, vol. 51, p. 83.
6. T. Fuyuki, T. Kobayashi, and H. Matsunami: *Jpn.: J. Appl. Phys.*, 1986, vol. 25, p. 1288.
7. K.S. Yeung and Y.W. Lam: *Thin Solid Films*, 1983, vol. 109, p. 169.
8. G.P. Burns, I.S. Baldwin, M.P. Hastings, and J.G. Wilkes: *J. Appl. Phys.*, 1989, vol. 66 (6), p. 2320.
9. T. Schneider, M. Baron, D. Edwards, R. Gandy, and J. Fukar: *J. Appl. Phys.*, 1990, vol. 67 (3), p. 1601.
10. Jian Zhang: Ph.D. Dissertation, University of Missouri-Rolla, Rolla, MO, 1994.
11. T.J. Nurse and F. Wormwell: *J. Appl. Chem.*, 1952, vol. 2, p. 550.
12. T. Fukuzuka, K. Shimogori, H. Satoh, and F. Kamikubo: *Titanium '80 Science and Technology*, Proc. 4th Int. Conf. on Titanium, 1980, Met. Soc. AIME, Warrendale, PA, vol. 4, p. 2782.
13. D.M. Mattax: *J. Vac. Sci. Technol.*, 1973, vol. 10 (1), p. 47.
14. J.-L. Delplancke and R. Winand: *Electrochim. Acta*, 1988, vol. 33 (11), p. 1539.
15. Gordon Skinner, Herrick L. Johnston, and Charles Beckett: *Titanium and Its Compound*, Herrick L. Johnston Enterprises, Columbus, OH, 1954, p. 21.
16. S. Andersson, B. Collen, U. Kuylenstierna, and A. Magneli: *Acta Chem. Scand.*, 1957, vol. 11, p. 1641.
17. Per Kofstad: *High-Temperature Oxidation of Metals*, John Wiley & Sons, Inc., New York, NY, 1966, pp. 169–78.
18. R.R. Dogonadze, A.M. Kuznetsov, and J. Zak: *Electrochim. Acta*, 1977, vol. 22, p. 967.
19. K.E. Heusler and Kyung Suk Yun: *Electrochim. Acta*, 1977, vol. 22, p. 977.
20. J.-L. Delplancke and R. Winand: *Electrochim. Acta*, 1988, vol. 33 (11), p. 1551.
21. J.-L. Delplancke, M. Sun, T.J. O'Keefe, and R. Winand: *Hydrometallurgy*, 1989, vol. 23, p. 47.
22. J.-L. Delplancke, M. Sun, T.J. O'Keefe, and R. Winand: *Hydrometallurgy*, 1990, vol. 24, p. 179.