*Journal of The Electrochemical Society*, **149** (3) G204-G208 (2002)
0013-4651/2002/149(3)/G204/5/$7.00 © The Electrochemical Society, Inc.

# The Removal Selectivity of Titanium and Aluminum in Chemical Mechanical Planarization

**Jyh-Wei Hsu,[a] Shao-Yu Chiu,[b] Ying-Lang Wang,[c] Bau-Tong Dai,[d] Ming-Shih Tsai,[d,*] Ming-Shiann Feng,[b] and Han-C. Shih[a,*,z]**

[a]*Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 300, Taiwan*
[b]*Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan*
[c]*Taiwan Semiconductor Manufacturing Company, Hsinchu 300, Taiwan*
[d]*National Nano Device Laboratories, Hsinchu 300, Taiwan*

The removal selectivity control of aluminum and titanium metal barrier during aluminum chemical mechanical polishing in the Damascene process is known to be critical for surface planarity without metal dishing and dielectric erosion. Unfortunately, the electrochemical behaviors of aluminum and titanium are dissimilar, as one may expect. In this study, *in situ* electrochemical impedance spectroscopy was carried out to investigate the influences of $H_2O_2$ concentration, slurry pH, and metal oxide formation through the passivation on aluminum and titanium. As $H_2O_2$ concentration increases, the measured impedance of aluminum and titanium decreases, or the oxidation rates of these two metals are enhanced upon increasing the oxidizer concentration. As the slurry pH increases, the removal rate of polished titanium increases, but it decreases for polished aluminum. The removal rate of titanium was limited to its oxidation rate and aluminum was limited to its oxide dissolution rate.
© 2002 The Electrochemical Society. [DOI: 10.1149/1.1449954] All rights reserved.

Manuscript submitted April 16, 2001; revised manuscript received October 19, 2001. Available electronically February 7, 2002.

Chemical mechanical polishing (CMP) has long been recognized as a promising technique for global planarization to delineate metal patterns for submicrometer integrated circuit (IC) processing.[1-3] Aluminum (Al) and its alloys have traditionally been used as multilevel interconnects and have emerged as the most important material for such applications. On the other hand, it is well known that titanium (Ti) is an effective metal barrier.[4] The total process time for Al CMP is also controlled by the removal of the Ti diffusion barrier. Little research has been devoted to the CMP of this barrier film. Since Ti is harder than Al, a lower Ti removal rate is therefore expected.

Because Al is soft and easily scratched, polishing on a softer pad has therefore been suggested to avoid severe surface damage, but this technique can produce unwanted pattern geometry effects like metal dishing and interlevel dielectric (ILD) erosion.[5] Therefore, a two-step CMP process has usually been implemented. For the first step, the overburden Al would be planarized for the step-high reduction, be removed faster and uniformly, and stopped as Ti exposed. For the second step, both Al and Ti outside of trenches would be removed simultaneously and stopped as the ILD exposed. The control of removal selectivity is therefore very critical in the second step. In the ideal case, Al, Ti, or TiN and ILD would be expected to remove at the same rate, or it would result in metal dishing, oxide erosion, and surface nonplanarity. Overpolishing for the complete removal of overburden metals outside of trenches would further induce surface nonplanarity.

Kaufman *et al.*[6] has proposed a desirable removal mechanism for metal CMP which involves the oxidation of metal to form passive surface oxide and dissolution of this metal oxide under polishing stress. No direct metal corrosion to form soluble metallic ions or direct mechanical abrasion on nonoxidized metal substrates would be allowed for CMP, and it would result in the issues of metal corrosion and surface scratching. The formation and dissolution of oxide passive film on a given metal surface would strongly depend on the oxidizing conditions in the aqueous media controlled by the slurry formulation.

One may obtain useful information regarding the thermodynamically stable oxidized species of Al and Ti metals in a given pH aqueous medium from Pourbaix diagrams,[7] but not enough for the complicated, dynamically removed and reformed metal oxide surface during the polishing due to the absence of any kinetic information. Both Al and Ti are reactive metals that owe their corrosion resistance to a thin, protective, barrier oxide surface layer which is stable in air and in most aqueous solutions. Regarding material removal during the metal CMP, the properties of the metal oxide on the surface is the key issue. But there is the question of whether the overall removal rate is limited to the oxidation rates of metal to form metal passive oxide, or the dissolution rates of this passive oxide into the aqueous slurry. Furthermore, both the rate of metal oxidation and the rate of metal oxide dissolution is modulated by the mechanical stress during polishing, like pressure, platen rotation velocity, and abrasive size.

Both the chemical and mechanical interactions should be taken into account simultaneously to elucidate the complicated material removal during polishing. There are two possible approaches to modeling the CMP process. One is to describe the CMP process as chemically assisted abrasion based on the contact wear between the abrasives and the substrate. The material removal is proportional to the volume of plastic deformation of substrate on which abrasive stress is imposed. The most difficult point of this approach, in practice, is how to determine the change of mechanical hardness of the chemically softened layer on substrate or abrasives in a given slurry chemical formulation. The other way is that the stress-modulated corrosion (or dissolution) based on the metal corrosion under a given slurry formulation and polishing stress could be well characterized by modern electrochemical techniques such as dc polarization and ac impedance methods. One may suspect that the overall removal could be contributed only from metal corrosion, not partly from abrasion wear. Removal by microdebris wearing could happen as if polishing with the larger particles on the harder pad, which is not an acceptable CMP process due to the severe surface damage. Therefore, it is reasonable and practical to explore metal CMP by *in situ* electrochemical corrosion measurements during the polishing.

In this work, electrochemical impedance spectroscopy (EIS) analyses of Al and Ti during polishing or in static conditions was performed to evaluate the influence of $H_2O_2$ and slurry pH on the surface passivation of Al and Ti. From these results, the control of removal selectivity between Al and Ti by means of slurry formulation is discussed.

## Experimental

The special designed apparatus based on the traditional three-electrode rotating-disk configuration for *in situ* CMP measurement is schematically shown in Fig. 1. The electrochemical cell consisted

* Electrochemical Society Active Member.
z E-mail: hcshih@mse.nthu.edu.tw

Downloaded on 2014-04-27 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

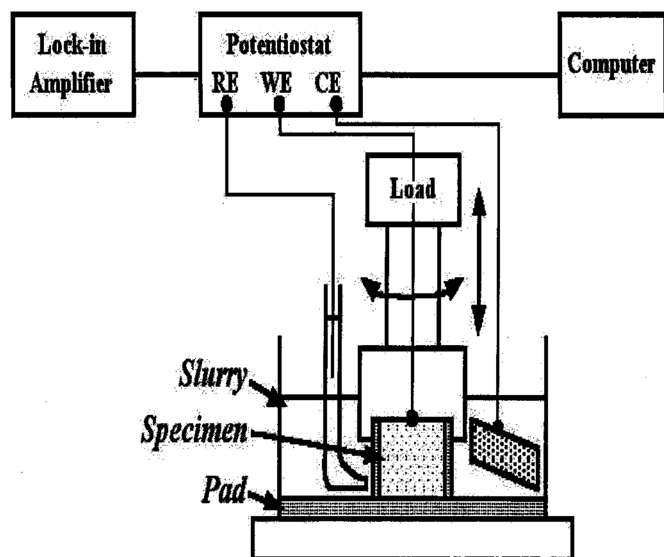


**Figure 1.** Schematic of the *in situ* electrochemical measurement system.

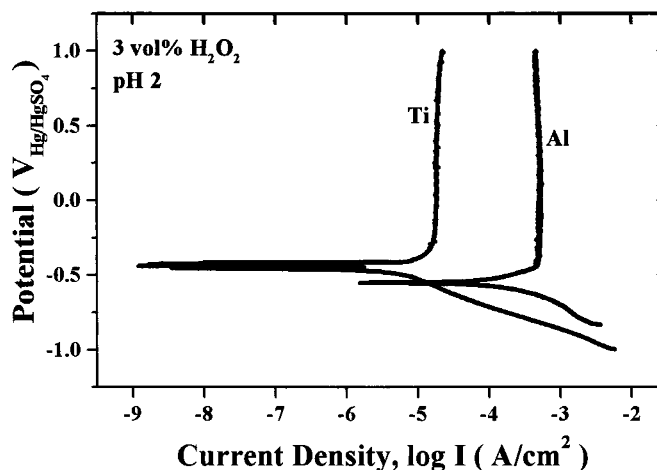


**Figure 2.** Potentiodynamic polarization curve for Ti and Al in a slurry of 3 vol % $H_2O_2$ at pH 2.

of a metal cylinder as the rotating working electrode and a Pt mesh net and an $Hg/HgSO_4$ half-cell electrode as the counter and reference electrodes, respectively. The three-electrode electrochemical cell was connected to an EG&G lock-in amplifier model 5301 and potentiostat model 273, and immersed in the slurry with a Rodel Politex regular E polishing pad at the bottom. The working electrodes were made of a Ti (99.99%) and Al (1% Si-0.5% Cu) cylinder embedded in epoxy resin ($1 \text{ cm}^2$); only one side of the cylinder was exposed to the slurry.

For EIS measurements, the polishing condition was fixed at a 45 rpm rotational speed and 4 psi downward pressure, the amplitude of the perturbation was $\pm 10$ mV, and the frequency varying from 0.1 Hz to 100 kHz at 6 steps/dec. The slurry used in the experiments contained 0.5 M citric acid and 5 vol % phosphoric acid as the pH buffer solution, 0.05 $\mu$m $Al_2O_3$ abrasive particles of 5 wt %, and 0-10 vol % $H_2O_2$ as the main oxidizer. The slurry pH was adjusted from 2 to 6 by adding KOH. Zview version 2.1a computer software was used for the curve fitting and analysis of the impedance.

Polishing experiments were carried out on a Westech 372M polisher with a Rodel Politex regular E polishing pad and Rodel R200-T3 carrier film. For the Al polishing process, the polishing parameters of pressure, platen and carrier rotary speeds, back pressure, and slurry flow rate were set to 4 psi, 60 and 65 rpm, 2 psi, and 150 mL/min, respectively. In the Ti polishing step, back pressure and slurry flow rate were the same as the Al polishing process, with platen and carrier rotary speeds adjusted to 45 and 42 rpm, respectively.

## Results and Discussion

*EIS for Ti without abrasion.*—Figure 2 shows the potentiodynamic polarization curves for Ti and Al in a slurry of 3 vol % $H_2O_2$ at pH 2. It is evident from these polarization curves that both Ti and Al show an excellent passivation behavior and the corrosion potential for Ti is considerably nobler than that for Al by 125 mV.

As exposed into the slurry of pH 2 without the addition of $H_2O_2$, the EIS of Ti shows the presence of a stable thin metal oxide layer formed on the surface, as shown in Fig. 3. Furthermore, the impedances only increase slightly with exposure time, indicating that this oxide is quite stable after 20 min. In contrast, the impedance decreases in the presence of $H_2O_2$; the higher the $H_2O_2$ is added, the more the impedance decreases, as shown in Fig. 4. The diameter of the frequency loop in the absence of $H_2O_2$ is significantly larger than those in $H_2O_2$-added slurry. This implies that the polarization resistance ($R_P$) of the Ti oxide decreases in the presence of $H_2O_2$. The fitted $R_p$ and capacitance ($C$) in terms of a single time-constant model composed of a RC parallel circuit are listed in Table I. Typically, a two time-constant model is adopted to represent the system of metal oxide passivation; one time-constant is associated with the oxide and the other with the electrical double layer formed on the oxide surface. However, the double layer response at higher frequencies is negligible in comparison with the whole surface oxide, so the impedances responding at the frequencies we have studied in the range from 0.1 Hz to 100 kHz (as observed in Fig. 3 and 4) can be considered as the oxide on metal surface.

The fitted capacitance ($C$) of passivation oxide decreases slightly with increasing $H_2O_2$ concentration (Table I). This could result as a more porous metal oxide film forms, in contrast to the denser oxide film formed without $H_2O_2$. Porous oxide passivation formed in $H_2O_2$ would also contribute to the lower polarization resistance

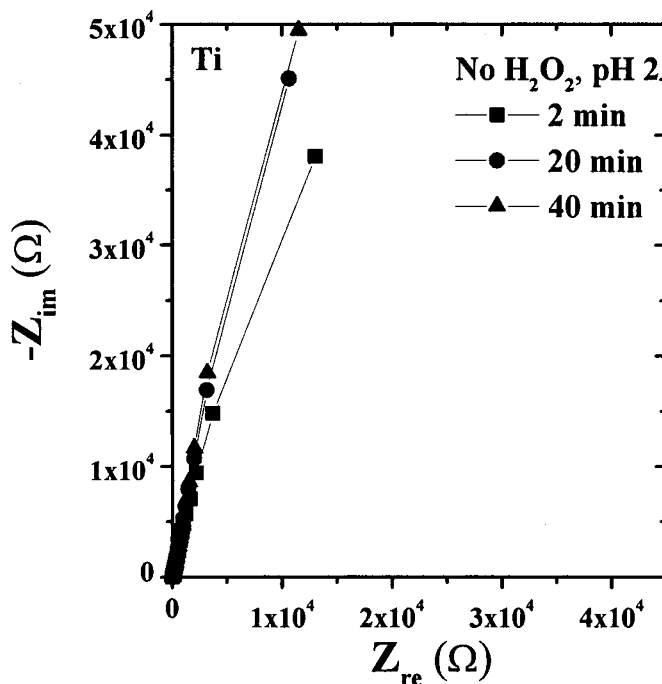


**Figure 3.** Nyquist plots for Ti experiencing various time intervals of immersion in a slurry of pH 2 without the addition of $H_2O_2$.

Downloaded on 2014-04-27 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

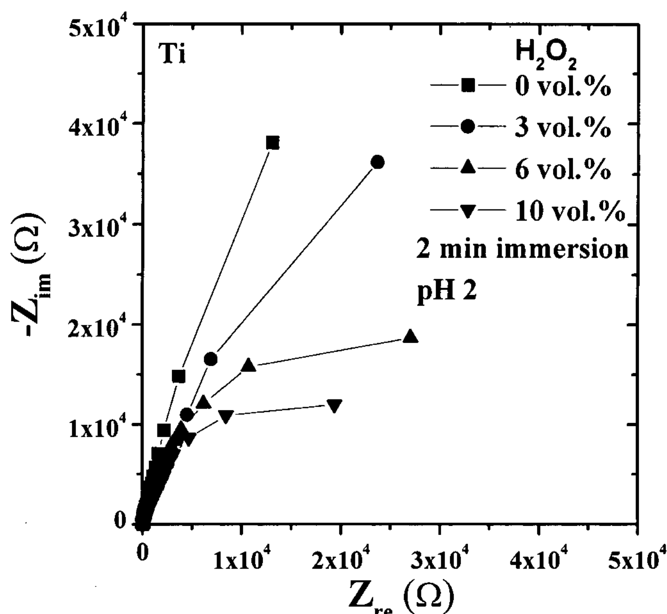


**Figure 4.** Nyquist plots for Ti in a slurry of pH 2 with various $H_2O_2$ concentrations after 2 min immersion.

($R_p$). This fact suggests that higher $H_2O_2$ concentrations would cause higher oxidation rates due to the formation of more porous oxide.[8-10] Similar results were also obtained for Al.[11]

*EIS for Ti with abrasion*.—The EIS of *in situ* measurements during polishing Ti in a slurry of 6 vol % $H_2O_2$ at pH 2 is shown in Fig. 5a. The impedances do not change with time for abrasion and are much smaller than those without abrasion as shown in Fig. 4. This means that the oxide could be almost removed by abrasion and may reach a dynamic equilibrium between the oxidation formation and the abrasion removal. Similar results were obtained for polishing Ti with 3-10 vol % $H_2O_2$ slurry at pH 2. In other words, the overall Ti removal rate is limited to its oxidation to form oxide, that is, more $H_2O_2$ added into the slurry to increase the Ti corrosion rate, so as to the removal rates of polishing Ti.

Figure 5b shows the EIS of the *in situ* measurements of polishing Al in the slurry with 6 vol % $H_2O_2$ at pH 2. The impedance ($R_P$) increases with abrasion time, indicating that the passive oxide exists and would not be removed completely, instead of growing with abrasion time. As a consequence, the Al removal rate is limited to the oxide dissolution. However, if $H_2O_2$ is lower than 3 vol %, the impedance does not change with abrasion time. In an ideal metal CMP process, the metal being polished should be oxidized fast enough to be equal to the acceptable removal rate.[12] Thus, a balance between the mechanical abrasion and the chemical reaction is believed to be the key issue for the metal CMP process. At low concentration, $H_2O_2$ increases the oxidation rate, resulting in an increase of the removal rate; however, for Al, excessive $H_2O_2$ concentration decreases the removal rate, since the oxidation rate exceeds the mechanical abrasion rate.

**Table I. Fitted parameters for Ti immersion in a slurry of pH 2 with various $H_2O_2$ concentrations.**

| Parameters $H_2O_2$ | 0 vol % | 3 vol % | 6 vol % | 10 vol % |
|---|---|---|---|---|
| Capacitance, $C$ (μF) | 33.9 | 29.5 | 23.7 | 22.5 |
| Resistance, $R_p$ (kΩ) | 3615.7 | 53.4 | 36.3 | 22.9 |

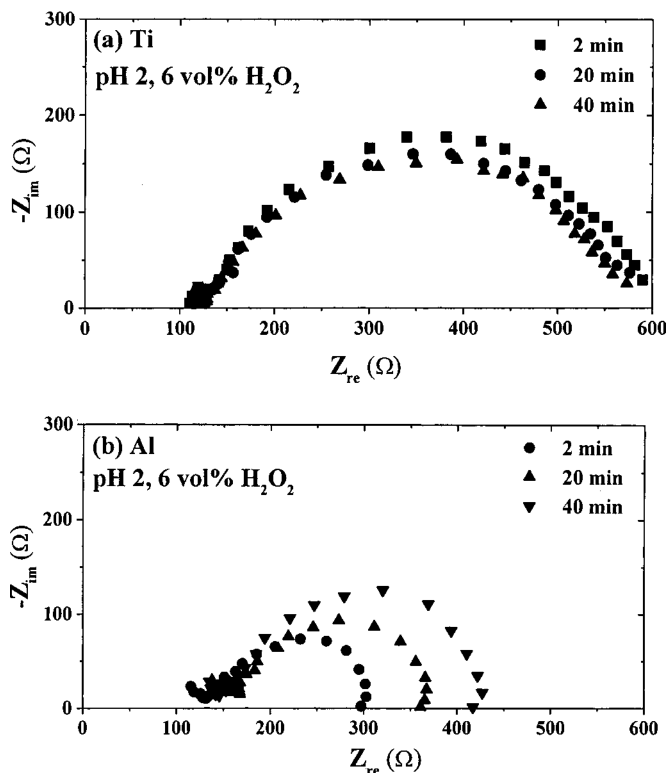


**Figure 5.** Nyquist plots after various time intervals of abrasion in a slurry of 6 vol % $H_2O_2$ at pH 2: (a) Ti and (b) Al.

In this study, the formation of metal oxide passivating the metal plays a crucial role for Al and for Ti CMP. In a given aqueous corrosion environment, metal being polished could be oxidized to form soluble species, *i.e.*, dissolution, or to form metal oxide through the passivation.

If dissolution dominates, removal rate is limited to the oxidation rate of metal being polished and behaves like wet etching. This is an unfavored condition for planarization and the surface damage, like roughness and scratches, and would be obtained due to direct abrasion on the soft metal substrate. In addition, no stable oxide after polishing would lead to severe metal corrosion for post-CMP cleaning. This is the typical problem for Cu CMP.[13]

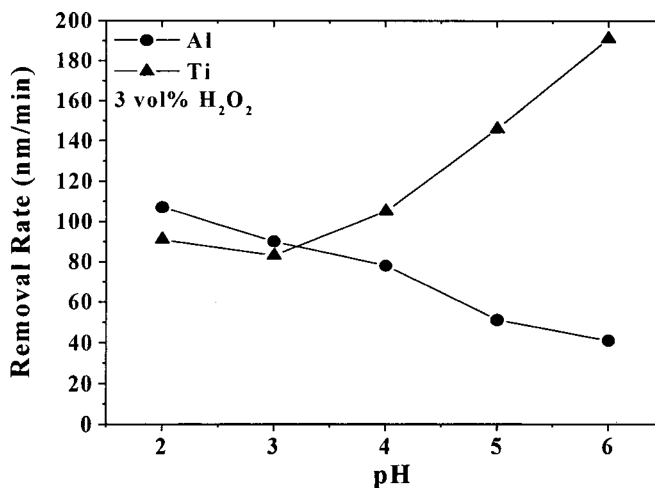


**Figure 6.** The removal rates of polishing Al and Ti with the slurry formulated with 3 vol % $H_2O_2$ at various slurry pH values.

Downloaded on 2014-04-27 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

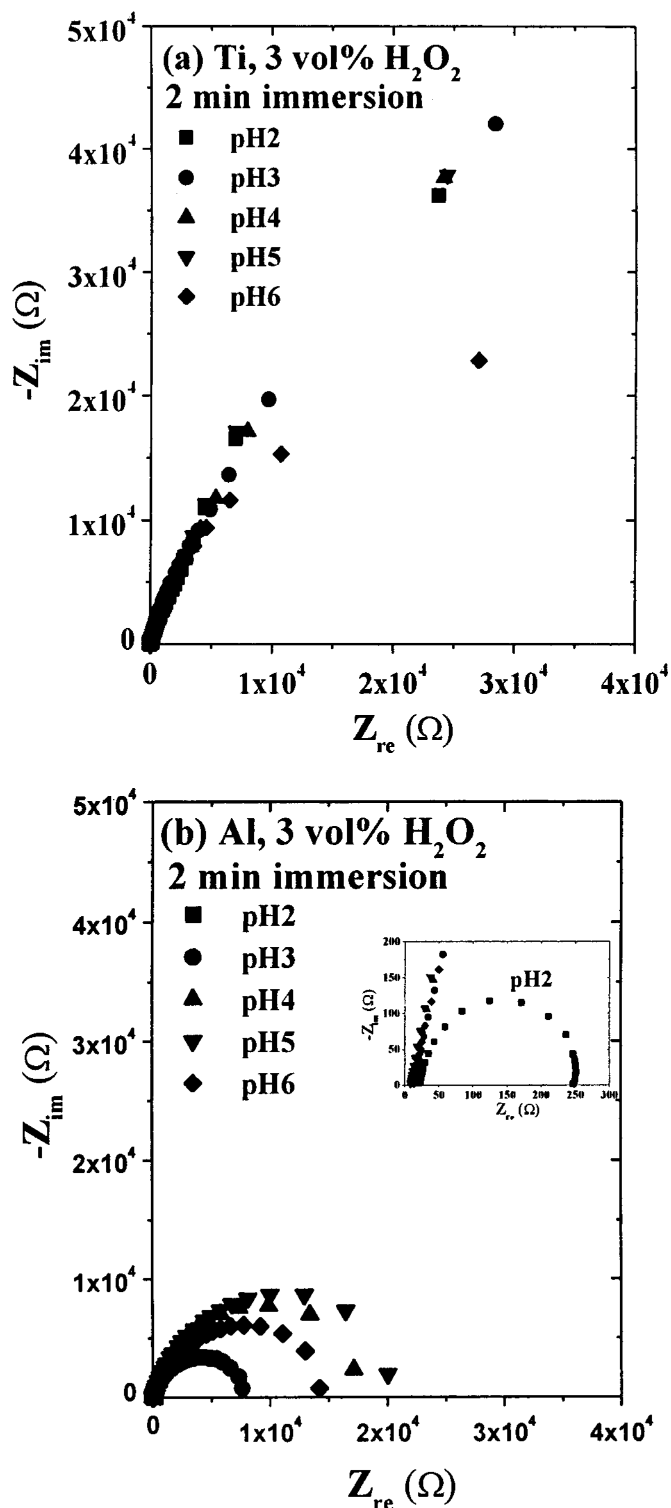


**Figure 7.** Nyquist plots of the specimens without abrasion in a slurry of 3 vol % $H_2O_2$ at various pH values after 2 min immersion: (a) Ti and (b) Al.

If oxidation dominates, removal rate would be limited to both the oxidation rate of metal and the dissolution rate of the oxide under the polishing stress. For polishing Ti and Al with hydrogen peroxide ($H_2O_2$) formulation, Ti removal is limited by the oxidation step to the formation of $TiO_2$. On the other hand, Al could be oxidized fast and form $Al_2O_3$ through the passivation of Al. The removal of Al is limited to the dissolution step of $Al_2O_3$ as a result of passivation.

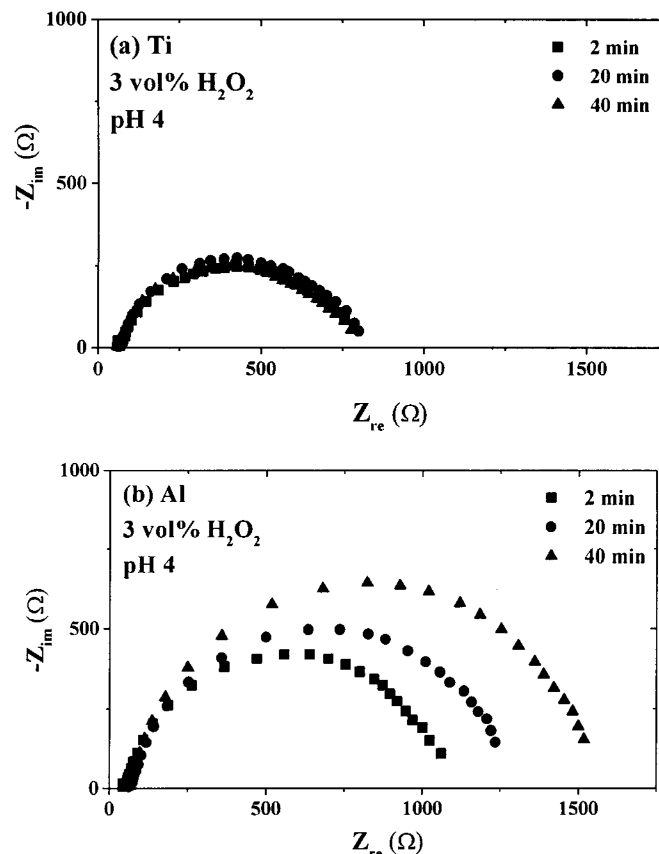


**Figure 8.** Nyquist plots for Ti after different time intervals of abrasion in a slurry of 3 vol % $H_2O_2$ at pH 4: (a) Ti and (b) Al.

*Effect of pH*.—If Ti could be removed faster than Al, overpolishing of Al would be shortened and the result of dishing could be reduced. The removal selectivity can be changed by means of polishing with various slurry pH values. Figure 6 shows that as slurry pH increases the removal rate of Al decreases, while that of Ti increases. At slurry pH $\geqslant$ 4, the removal rate of Ti is notably faster than that of Al, and in the range of slurry pH 3.0-3.5 the Al/Ti removal selectivity is expected to be unity. However, the unity removal selectivity of blanket Al/Ti is undesirable for a practically polished patterned wafer. Indeed, the removal of Ti outside the trenches on the larger oxide features would be slower than those of dense Al interconnecting wires, and result in Al dishing as overpolishing to remove Ti completely.

Figures 7a and b are Nyquist plots for Ti and Al without abrasion as varying with slurry pH with the addition of 3 vol % $H_2O_2$ after 2 min of immersion. These plots indicate that the electrochemical reactions are different but depend on the slurry pH. Figure 7a shows clearly that impedance decreases in slurry pH 6. On the contrary, for Al, as shown in Fig. 7b, impedance increases as slurry pH increases to 5 but drops at pH 6, exhibiting that the passivation on Al would be maximized between pH 5 and 6. Consequently, increasing the slurry pH enhances the dissolution rate of Ti but decreases the dissolution rate of Al.

An *in situ* measurement for Ti in a slurry with addition of 3 vol % $H_2O_2$ at pH 4 is shown in Fig. 8a. The EIS spectra do not change with time of abrasion appreciably, and similar results are also obtained for slurry pH from 2 to 6. The dissolution rate of $TiO_2$ is faster than oxidation rate of Ti. On the other hand, the result of impedance for Al increases with time of abrasion, as shown in Fig. 8b, indicating that the oxides are not removed completely, becoming stable and dense and difficult to remove. Hence, the oxide dissolution rate is lower than the oxidation rate of Al. Then the by-products

Downloaded on 2014-04-27 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

of the polishing may not be dissolved into the slurry and tend to be redeposited onto the surface.[14] Furthermore, Al surface tarnishing appearance after abrasion is a result of a thin oxide that forms on the surface. Some interesting results show that the impedance of Ti is smaller than that of Al as the removal rate of Ti is faster than Al, while the corrosion rate of Ti is higher than that of Al. Consequently, because the removal rate of Al is slower than that of Ti, and the Al in the trench should have been protected during the second step of Ti polishing, the metal dishing could therefore be inhibited.

## Conclusions

1. EIS is a powerful technique for *in situ* characterization of the passive film and has been applied to the study of the $H_3PO_4$-$H_2O_2$ based slurry for Al and Ti CMP.

2. For both Ti and Al, impedance decreases with the addition of $H_2O_2$, indicating an increase of corrosion rate.

3. Ti removal rate is limited to its oxidation and to form an oxide passivation; Al removal rate is limited to the oxide dissolution.

4. With an increase of the slurry pH, impedance decreases for Ti but increases for Al. Correspondingly, increasing the slurry pH value enhances the Ti removal rate but decreases the Al removal rate. The Al/Ti removal selectivity is expected to be unity in the slurry pH 3.0-3.5 range with 3 vol % $H_2O_2$.

## Acknowledgment

The authors are grateful for support of this work by the National Science Council (NSC) of Republic of China under grant NSC 89-2218-E-007-005.

*National Tsing Hua University assisted in meeting the publication costs of this article.*

## References

1. S. Sivaram, H. Bath, R. Leggett, A. Maury, K. Monning, and R. Tolles, *Solid State Technol.,* **35**, 87 (1992).
2. P. H. Singer, *Semicond. Int.,* **1992**, 44 (March).
3. R. Iscoff, *Semicond. Int.,* **1993**, 72 (May).
4. S. Thomas and H. M. Berg, *IEEE Trans. Compon., Hybrids, Manuf. Technol.,* **CHMT-10**, 252 (1987).
5. J. M. Steigerwald, R. Zirpoli, S. P. Murarka, D. Price, and R. J. Gutmann, *J. Electrochem. Soc.,* **141**, 2842 (1994).
6. F. B. Kaufman, D. B. Thompson, R. E. Broadie, M. A. Jaso, W. L. Guthrie, D. J. Pearsons, and M. B. Small, *J. Electrochem. Soc.,* **138**, 3460 (1991).
7. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, NACE, Houston, TX (1974).
8. D. Tengvall, H. Elwing, L. Sjöqvist, I. Lundström, and L. M. Bjursten, *Biomaterials,* **10**, 118 (1989).
9. D. Tengvall, H. Elwing, L. Sjöqvist, I. Lundström, and L. M. Bjursten, *Biomaterials,* **10**, 166 (1989).
10. J. Pan, D. Thierry, and C. Leygraf, *Electrochim. Acta,* **41**, 1143 (1996).
11. J. W. Hsu, S. Y. Chiu, I. C. Tung, Y. L. Wang, B. T. Dai, M. S. Tsai, M. S. Feng, and H. C. Shih, in *Chemical Mechanical Planarization in IC Device Manufacturing III*, R. L. Opila, I. Ali, Y. A. Arimoto, Y. Homma, C. Reidsema-Simpson, and K. B. Sundaram, Editors, PV 99-37, p. 311, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).
12. L. M. Cook, J. F. Wang, D. B. James, and A. R. Sethuraamn, *Semicond. Int.,* 141 (Nov 1995).
13. A. Beverina, H. Bernard, J. Palleau, J. Torres, and F. Tardif, *Electrochem. Solid-State Lett.,* **3**, 156 (2000).
14. J. M. Steigerwald, S. P. Murarka, D. J. Duquette, and R. J. Gutmann, *Mater. Res. Soc. Symp. Proc.,* 133 (1994).

Downloaded on 2014-04-27 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).