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The application of electrochemical metrologies for investigating chemical mechanical polishing of Al with a Ti barrier layer

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Abstract

In situ electrochemical measurements were performed for Al and Ti disks in various slurries during polishing and static conditions. The electrochemical results obtained from the corrosion potential drop of Al polishing have verified that the maximum removal rate of metal CMP can be achieved when the removal rate of the surface oxide was equal to its growth rate. However, Ti polishing did not exist maximum removal rate. The effects of H_2O_2%, pH values and pressure on the Al and Ti polishing behaviors were explored by using potentiodynamic scan. The corrosion potential drop was found to be a good index for polishing removal rate. The corrosion potential drop changed with increasing H_2O_2% for Al polishing and there existed a maximum value. But the corrosion potential drop increased with increasing H_2O_2% for Ti polishing. The pH value had different effects on Al and Ti polishing. Higher pH values gave higher Al removal rate but lower Ti removal rate. The Al polishing showed more pressure sensitive than Ti polishing did. The galvanic current was measured for Al/Ti polishing. For slurry with 6 vol.% H_2O_2 and pH = 4, the abraded Al electrode obtained a negative current, which implied Ti oxidation was enhanced.
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Keywords: Chemical mechanical polishing; Aluminum; Titanium; Selectivity

1. Introduction

Chemical mechanical polishing (CMP) has been widely accepted as an emerging key technology for achieving global planarization for interlevel dielectric (ILD) and damascene processes in the deep sub-micron multilevel interconnect fabrication. Compared with conventional subtractive etched metallization, CMP of patterned aluminum (Al) lines in a damascene process gives inherent surface planarity, better interconnect reliability (compared to Al wire/W plug structures), and simplified process, which imply its low cost of ownership [1–5]. Therefore, Al alloys, which have been used as interconnects for more than 30 years, are still being extensively investigated because of their pervasive presence in manufacturing and extendibility into damascene processes for 0.13–0.18 μm CMOS technology.

Due to the soft nature of Al alloys, compared to tungsten or copper, Al CMP meets great challenges to achieve good structural planarity and minimum surface scratch density [1,6]. The mechanisms of metallic CMP are very complicated. Because of these difficulties, in order to obtain a better understanding and control of Al CMP, the electrochemical behavior of metal in a given slurry environment during polishing should be explored. To this end, conventional electrochemical analytical techniques of metal corrosion characterization have been adopted and modified for studying the dynamic metal oxidation and dissolution during polishing, it would be the basis for development of appropriate slurry formulation for a successful Al CMP [7–9].

The total process time for Al CMP is controlled by the removal rates of both Al and its barrier layer. Titanium (Ti) is known to be an effective barrier/adhesion or wetting layer (liner metal) for Al metallization [10–12]. Accordingly, removal selectivity between Al and Ti is critical in determining the yield and throughput of Al CMP. In addition, passive corrosion during the overpolish time may lead to corrosion and recess of the Al structure. Therefore, the understanding

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of how the Al/Ti removal selectivity is affected by the slurry chemistry is of great importance.

In this study, our investigations were concentrated on the polishing of Al alloys coupled with Ti in phosphoric acid and hydrogen peroxide based slurries [13]. The electrochemical methods, including the potentiodynamic polarization and galvanic corrosion measurements, have been used to elucidate the electrochemical mechanism for the removal selectivity in Al CMP.

2. Experimental

The slurry under investigation was formulated [13] with 5 wt.% EXTEC™ XL-16761 γ-Al_2O_3 abrasive (0.05 μm in size, 3.14 g cm^{-2} in density), 5 vol.% phosphoric acid (H_3PO_4), and hydrogen peroxide (H_2O_2) (0–10 vol.%) in acidic aqueous solutions. Slurry pH was buffered with 0.5 M citric acid [(COOH)(OH)C(CH_2COOH)$_2$] and adjusted with adding variable amounts of 0.5 N potassium hydroxide (KOH) aqueous solutions.

The electrochemical measurements were performed in three runs using commercial pure Al–1% Si–0.5% Cu (99.7%) and/or Ti (99%) cylinder with a diameter of 0.8 cm (embedded in epoxy resin) as working electrodes on an EG&G potentiostat/galvanostat Model 273. The mixed corrosion potential was measured with respect to a standard Hg/$HgSO_4$ electrode [+640 mV w.r.t. standard hydrogen electrode (SHE)] as a reference electrode. The conductor electrode was platinum (Pt). The potentiodynamic scans were performed at a rate of 1 mv s^{-1} from 0.25 V below the open circuit potential to 1.0 V. The corrosion current density was determined by Tafel's extra-polation technique [14]. In order to trace the electrochemical behavior with abrasion and without abrasion, the working electrode was kept rotating at 300 rpm, regardless of whether abrasion was present on a Rodel Politex regular E polishing pad. During polishing, a down force of 4 or 8 psi was selected to be applied to the abraded metal surface. The setup used for potentiodynamic measurements was the same with that proposed by Kneer et al. [15]. From the potentiodynamic scans, the changes in the mixed potentials between the non-abraded and abraded electrodes and the current densities in both cases were extracted.

The other novel equipment designed for in situ electrochemical measurements during polishing is schematically shown in Fig. 1. This setup consists of two working electrodes, the Al alloys and Ti, with the slurry as the electrolyte. When auxiliary (AUX) and reference (REF) terminals are shorted, the potentiostat would control potential between two working electrodes at any specified value [14]. If that value is set at zero, the circuit would continuously and automatically read the galvanic couple current from the potentiostat zero resistance ammeter. It thus offers the capability of performing both the in situ polishing and static conditions for galvanic corrosion measurements. Following the electrochemical theory, the galvanic current flow is a result of the different electrochemical potentials between the two working electrodes in the slurries [14].

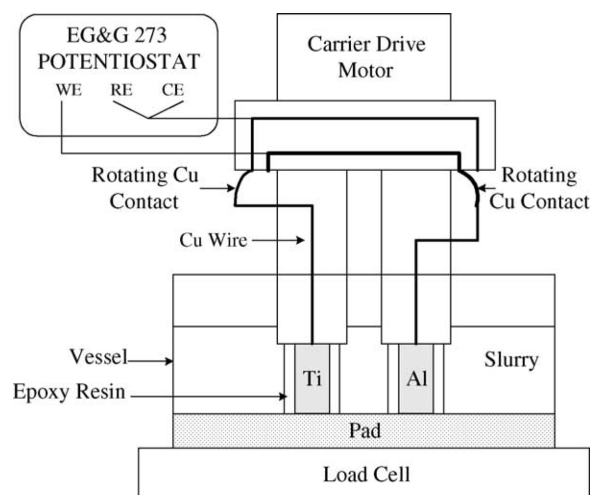

Fig. 1. Schematic of the in situ electrochemical apparatus for measuring galvanic current.

The blanket wafer polishing experiments were carried out on a Westech 372 M polisher using Rodel Politex regular E polishing pads and R200-T3 carrier film. Polishing parameters, such as pressure, platen and carrier rotary speeds, back pressure, slurry flow rate were set to be 5 psi, 45 rpm, 42 rpm, 2 psi, and 150 ml min^{-1}, respectively. Removal rates were calculated from the sheet resistance measured with Tencor M-Gage inductive current method for both the stacked SiO_2/Ti/Al–1% Si–0.5% Cu layer, about 550/40/900 nm in thickness, and the SiO_2/Ti stacked layer, 550/400 nm, deposited on p-type, 100-orieted, 150 mm diameter silicon wafers.

3. Results and discussion

The mechanism for phosphoric acid and hydrogen peroxide-based Al CMP slurry has been early proposed in a US patent [13]. As proposed in that patent, the hydrogen peroxide is a weak acid added as an oxidant to the polished metal, and the phosphoric acid then etches the oxide while the slurry abrasive mechanically abrades the metal surface. In what follows, the effects of H_2O_2, pH values and applied pressures on the Al and Ti polishing rates will be extensively elucidated.

3.1. H_2O_2 concentration effects on Al removal behavior

Fig. 2 showed the potentiodynamic scans for Al tested in the slurries with 0 and 3 vol.% H_2O_2 at pH = 2. The difference in the corrosion potential and current density between the abraded (with a down force of 4 psi) and non-abraded electrodes [16] was small for 0 vol.% H_2O_2. This indicated

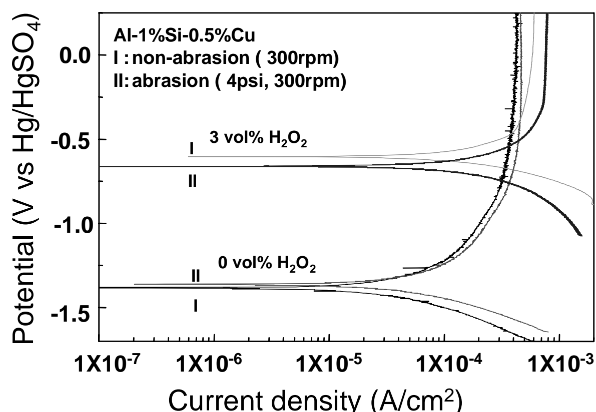

Fig. 2. Polarization curves for the Al electrode in the formulated slurries containing 0 or 3 vol.% H_2O_2 concentration at pH = 2, under non-abraded or abraded condition.

that the mechanical abrasion made very little contribution to the corrosion rate. Therefore, in the absence of H_2O_2, by referring to the Pourbaix diagram of aluminum water system [17], the removal rate would be apparently limited by the oxidation of Al ($Al + 3/2H_2O \rightarrow 1/2Al_2O_3 + 6H^+ + 6e^-$) and the dissolution of passivation oxide ($3/2Al_2O_3 + 3H^+ \rightarrow Al^{3+} + 3/2H_2O$). The addition of H_2O_2 decreased the corrosion potential but increased the current density. These results indicated that the passivating layer should be continuously formed and removed by the mechanical abrasion during the polishing process [18,19]. When H_2O_2 was added, unpassivated or exposed fresh Al reacted quickly with the free oxygen atom released from HO_2^- radicals ($H_2O_2 \rightarrow HO_2^- + H^+$) and the alumina oxide (Al_2O_3) formed ($Al + 3HO_2^- + 3H^+ \rightarrow 1/2Al_2O_3 + 3H_2O$). Then, the Al_2O_3 was hydrated and dissolved readily in the acidic environment ($3/2Al_2O_3 + 3H^+ \rightarrow Al^{3+} + 3/2H_2O$), contributing a high corrosion current density.

Fig. 3 showed the removal rates of Al CMP and the corresponding corrosion potential drop (ΔE) for various concentrations of H_2O_2. It was clear that ΔE and removal rate had the same trends when varying H_2O_2%. The maximum removal rate was achieved when the polishing rate of the passivating layer was equal to its growth rate. When the H_2O_2% was lower than ~3 vol.%, the polishing rate of the passivating layer would be higher than its growth rate. Thus, all passivating layer was removed and the removal rate of the Al CMP was limited by Al oxidation rate. The removal rate of Al CMP increased with increasing H_2O_2%. However, when the H_2O_2% was higher than ~3 vol.%, the polishing rate of the passivating layer would be slower than the oxidation rate. The Al CMP removal rate became limited by the mechanical abrasion or chemical erosion. The removal rate of Al CMP decreased with increasing the H_2O_2%.

3.2. H_2O_2 concentration effects on Ti removal behavior

Fig. 4 plotted the potentiodynamic scans for Ti tested in the slurries with 0 and 3 vol.% H_2O_2 at pH = 2. For non-abrasion, there was a slight increase in both the corrosion potential and current density by adding 3 vol.% H_2O_2. This presented that H_2O_2 enhanced the Ti oxidation rate (the increase in current density) and the formation of the passivating layer (the rise of corrosion potential). When the mechanical abrasion was applied, a prominent drop in the corrosion potential and a dramatic increase in the current density were found. This manifested that the mechanical abrasion improved the removal of the passivating layer and increased the Ti oxidation rate. In the absence of H_2O_2, the Ti was able to form a more effective passivating layer on

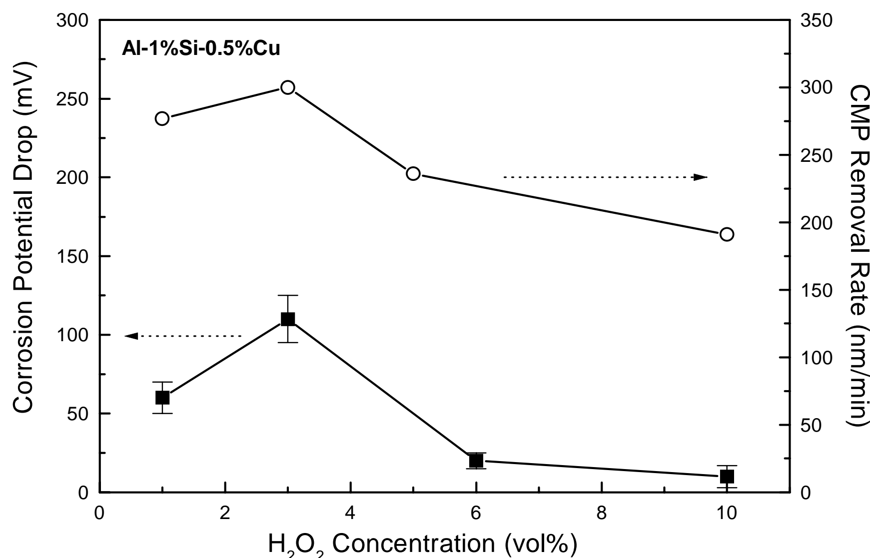

Fig. 3. Corrosion potential drops and removal rate of the Al electrode as a function of H_2O_2 concentration in the formulated slurries.

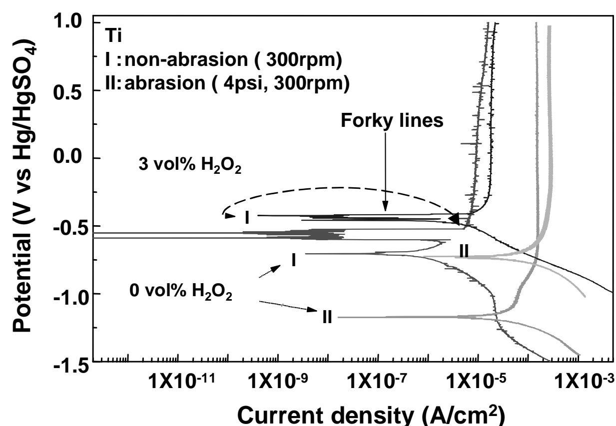

Fig. 4. Polarization curves of the Ti electrode in the formulated slurries containing 0 or 3 vol.% H_2O_2 concentration at pH = 2, under non-abraded or abraded condition.

its surface in the acidic slurry at pH = 2 due to the present of ΔE. Under the static condition, the forky lines along the potentiodynamic curve at about the corrosion potential were observed in Fig. 4. The forky lines were caused by the passivating layer, which should be highly efficient to protect the Ti metal against corrosion [7]. Fig. 4 also displayed that the addition of H_2O_2 reduced the efficiency of the passivating layer. The forky line regime got narrower with the addition of 3 vol.% H_2O_2. However, under the abrasion condition, the potentiodynamic curve turned to be smooth. This represented that the mechanical abrasion could significantly destroy the efficiency of the passivating layer.

The corrosion potential drop (ΔE) and CMP removal rate for Ti films were plotted against the H_2O_2% in Fig. 5. The ΔE increased for $H_2O_2 < 3\%$ and then nearly saturated for $H_2O_2\% > 3\%$. The removal rate was greatly increased with the increasing H_2O_2% until 6% is reached and then gradually levels off. The presence of the ΔE clearly indicated that the passivating layer was formed and then removed continuously during polishing. Besides, the polishing rate of the passivating layer should be higher than its growth rate. This was the reason why the polishing rate inevitably increased with the increasing H_2O_2%. The higher H_2O_2% gave higher Ti oxidation rate and hence removal rate was increased.

3.3. H_2O_2 concentration effects on Al/Ti removal selectivity

To ensure that there is no residual Al and adhesion/barrier metal Ti between the trenches in the damascene structure, the over-polishing of the wafer is hardly avoided. In such case, in order to eliminate defects arising from inefficient removal of the adhesion/barrier layers, it is essential to use slurry that possesses high enough removal rate selectivity to dielectric and preferable a 1:1 selectivity to the metal overlayer. Therefore, one of the resolutions to avoid Al defect (dishing or corrosive attack) is to adjust the slurry chemistry for the removal rate of Al CMP being close to that of Ti CMP. By comparing Figs. 3 and 5, the removal rates of Al and Ti became closer when the H_2O_2% increased. When adding 10% H_2O_2, the polishing selectivity of Al/Ti was approximately 3/2. This indicated that the polishing selectivity of Al/Ti was greatly improved by changing the H_2O_2%.

The removal mechanism of metal in the phosphoric-hydrogen peroxide-based slurry has been generally proposed [13]. The hydrogen peroxide oxidizes the metal, and acid then etches the oxide while the slurry abrasive mechanically abrades the surface. The current density obtained from the in situ electrochemical measurements during polishing

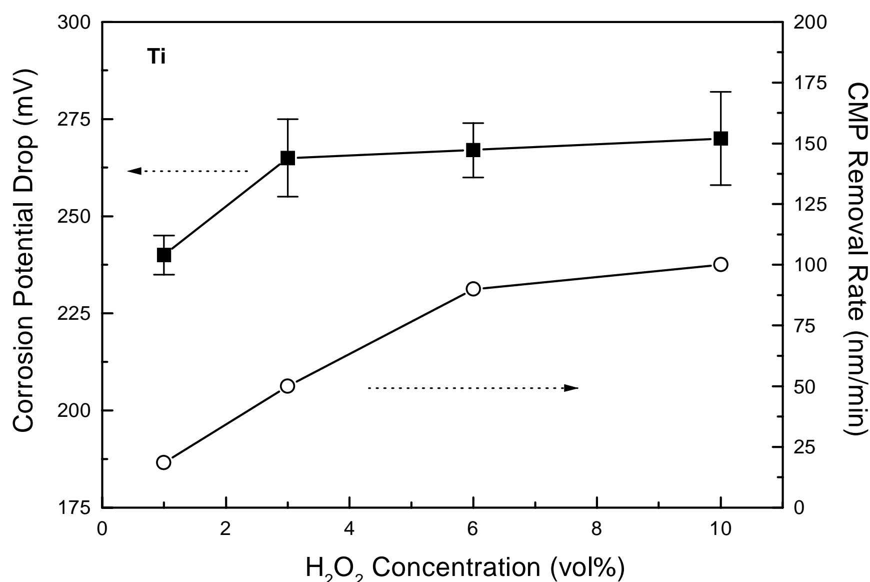

Fig. 5. Corrosion potential drops and removal rate of the Ti electrode as a function of H_2O_2 concentration in the formulated slurries.

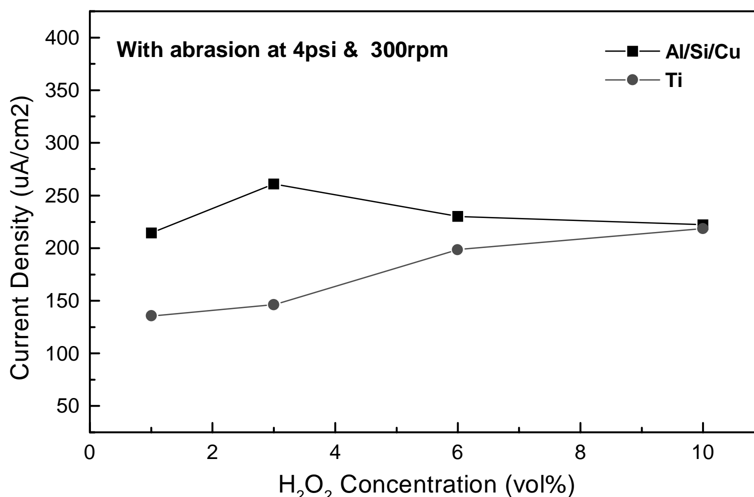

Fig. 6. Current densities of the Al and Ti electrodes as a function of H_2O_2 concentration in the formulated slurries under abrasion.

can thus be regarded as the indication of the removal rate of Al or Ti. The current densities with the abraded Al and Ti varying with the H_2O_2% were shown in Fig. 6. The current densities of Al and Ti became closer with increasing H_2O_2% and was equal at ∼10 vol.% H_2O. The current densities show the similar trend to the removal rates of Al and Ti in Figs. 3 and 5. Therefore, the current density of the abraded metal measured by the in situ electrochemical measurements can potentially be used to trace the removal rate of metal CMP.

3.4. pH effects on Al and Ti removal rates

Figs. 7 and 8 showed the potentiodynamic scans of the Al and Ti electrodes with the addition of 6 vol.% H_2O_2 at pH = 2 and 4, respectively. For Al electrode, the corrosion potentials were approximately at the same level for both the abrasion and non-abrasion condition. The current densities were lower for the samples tested at pH = 4 compared to those at pH = 2. Fig. 7 exhibited that the removal rate of Al CMP decreased with increasing pH values. The reasons were explained as following: at higher pH values, the Al direct dissolution tended to decrease. The oxide became more stable and was difficult to dissolve in the slurry. For Ti electrode, as shown in Fig. 8, the current densities remained unchanged with increasing pH values, whether under abrasion or not. This indicated that the corrosion or limiting current density degradation of Ti was insensitive to pH values. The removal rate of Ti was mainly limited by the oxidation rate. However, the corrosion potentials decreased with increasing pH values, indicating that the passivating capability was decreased with increasing pH values. This decrease in the corrosion potential clearly could not be suggested due to the decrease in oxidation rate ($Ti + 2H_2O_2 \rightarrow TiO_2 + 2H_2O$). However, it was suggested due to the less protective oxide formed by the dissolution reaction of TiO_2 ($TiO_2 + OH^- \rightarrow$

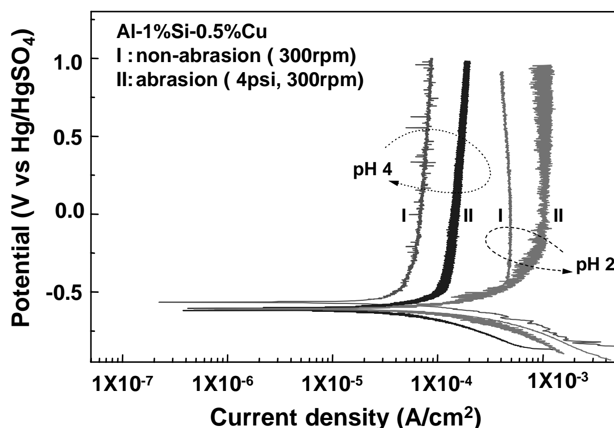

Fig. 7. Polarization curves for the Al electrode in the formulated slurries containing 6 vol.% H_2O_2 at pH = 2 or 4, under non-abraded or abraded condition.

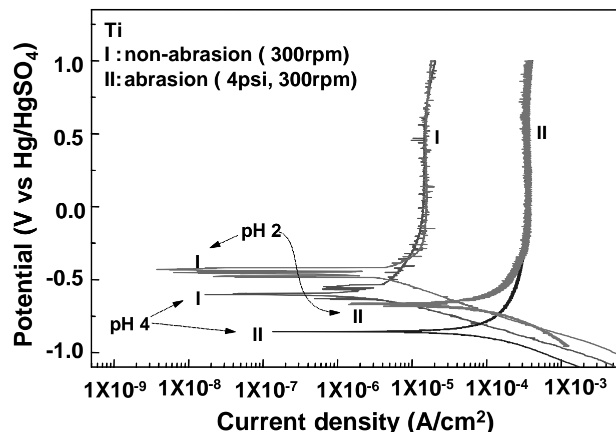

Fig. 8. Polarization curves for the Ti electrode in the formulated slurries containing 6 vol.% H_2O_2 at pH = 2 or 4, under non-abraded or abraded condition.

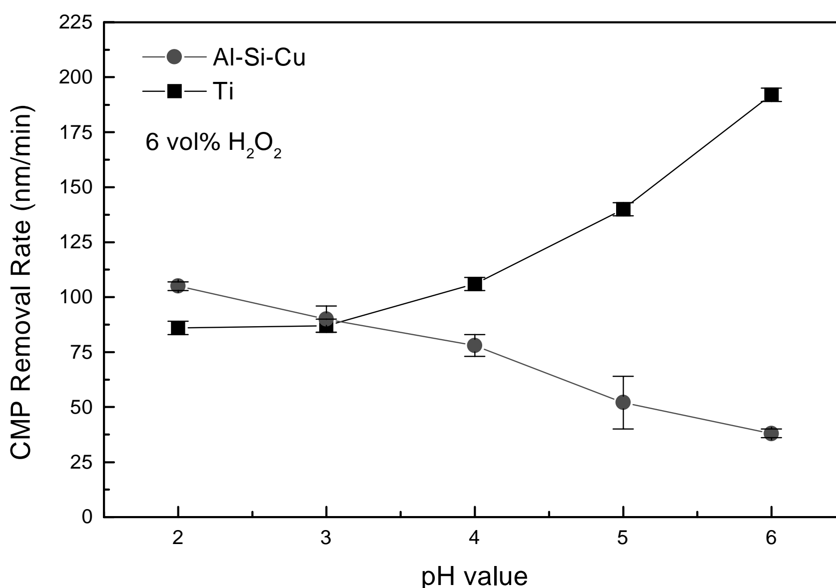

Fig. 9. The removal rate of polishing Al alloy and Ti with the slurry formulated with 6 vol.% H_2O_2 at various slurry pH values.

$HTiO_3^-$) with increasing pH values. Consequently, the oxide of polishing Ti surface became increasingly porous and hydrated, thereby producing an overall increase in CMP removal rate. Fig. 9 showed the CMP removal rate at different pH values. Higher pH values gave lower Al removal rate but higher Ti removal rate.

3.5. Pressure effects on Al/Ti removal selectivity

The potentiodynamic polarization curves of Al and Ti in the presence of 6% H_2O_2 at pH = 4 and different pressure were plotted in Figs. 10 and 11. For Al electrode, as the pressure increased to 4 psi, the current density increased but the corrosion potential had little change. When the pressure increased to 8 psi, a further increase in the current density and an obvious corrosion potential drop were observed. The mechanical abrasion at 8 psi caused a larger removal rate of surface oxide and naturally lead to a larger ΔE by degrading significantly the passivating capability. Therefore, this was the reason why the current density at 8 psi was much higher than that at 4 psi. This fact implied that mechanical abrasion was very helpful in oxide dissolution, thus leading to an obvious increase in the current density. For Ti electrode, both the current density and corrosion potential increased considerably when pressure was 4 psi as shown in Fig. 11. However, when the applied pressure increased further to 8 psi, the corrosion potential remained almost unchanged but the current density increased further. These results indicated that mechanical abrasion enhanced the Ti oxidation rate. All the passivating layer was nearly removed once it formed at the lower applied pressure 4 psi. Fig. 11 yielded that the removal rate of Ti was greatly increased once the

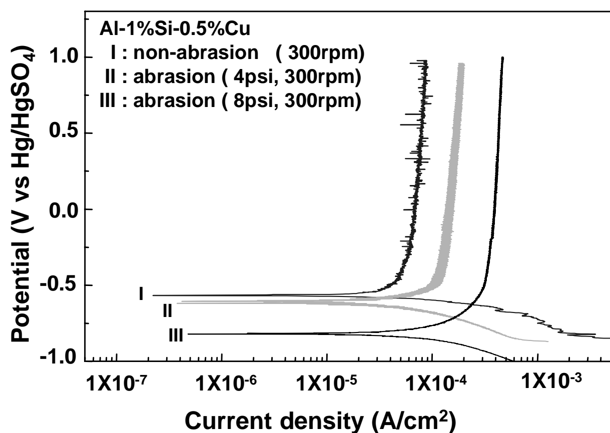

Fig. 10. Polarization curves for the Al electrode in the formulated slurries containing 6 vol.% H_2O_2 at pH = 4, under 4 or 8 psi abraded condition.

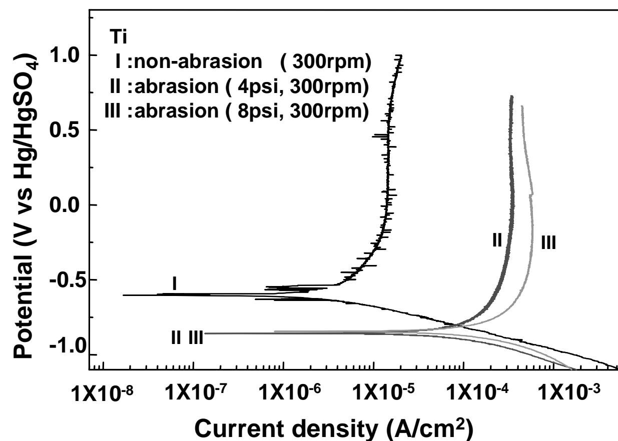

Fig. 11. Polarization curves for the Ti electrode in the formulated slurries containing 6 vol.% H_2O_2 at pH = 4, under 4 or 8 psi abraded condition.

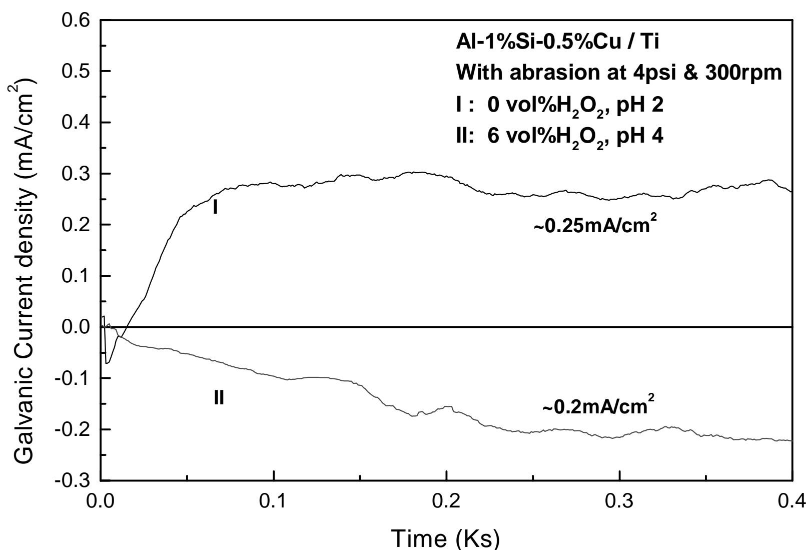

Fig. 12. The galvanic current between the abraded Al and Ti electrodes in the formulated slurries containing 0 vol.% H_2O_2 at pH = 2 and 6 vol.% H_2O_2 at pH = 4.

pressure was applied but only increased slightly when more pressure was further applied. This represented that the Ti passivating layer was easily removed. From the above results, the increase in the applied pressure was not favorable to Al/Ti polishing selectivity, because Al removal rate was not be further decreased. However, the difference behaviors of Al and Ti under high-applied pressure polishing gave the strong evidence for the competition model between the passivation and mechanical abrasion mention above.

3.6. Galvanic current measurements

The galvanic corrosion theory presents that a potential difference contributes a driving force for corrosion [14]. Fig. 12 showed the galvanic current between the abraded Al and Ti electrodes [20]. The abraded Al electrode obtained a positive current, which meant that Al oxidation was enhanced by the Al/Ti galvanic couple when pH value was 2 and no H_2O_2. Conversely, the abraded Al electrode obtained a negative current in the slurry containing 6 vol.% H_2O_2 at pH = 4. This indicated that the Ti oxidation was enhanced. In this particular case, the Al oxidation rate was suppressed, which was therefore fairly helpful to mitigate the Al dishing for polishing the Al/Ti patterned wafer.

4. Conclusions

The electrochemical studies on the Al and Ti abraded with the phosphoric acid and hydrogen peroxide-based Al CMP slurry containing Al_2O_3 abrasive were performed. The electrochemical results showed that the concentration of H_2O_2 affected the Al oxidation rate and the polishing rate. There existed one optimal H_2O_2 concentration to make the Al oxidation rate equal to the removal rate of the surface oxide. When this happened, the maximum removal rate of Al CMP was obtained. The Ti oxidation rate was lower than the removal rate of the oxide for all tested H_2O_2 concentrations. When the polishing rate of the passivating layer is higher than its growth rate, the pressure applied to the polished surface showed little increase in the corrosion potential drop for both the Al and Ti polishing. When the polishing rate of the passivating layer is lower than its growth rate, the increasing pressure applied to the polished surface will further increase the corrosion potential drop. With the addition of 6 vol.% of H_2O_2, the Al/Ti removal selectivity was improved with increasing slurry pH value. In this study, the novel equipment for in situ galvanic measurements was also successfully designed for evaluating the Al/Ti galvanic couple. It was found that Al oxidation was suppressed in the slurry with the addition of 6 vol.% H_2O_2 at pH = 4, compared to that at pH = 2 without addition of H_2O_2. In consideration of the Al/Ti removal selectivity, the polishing at pH = 4 with the addition of 6 vol.% H_2O_2 favorably mitigated the Al dishing or corrosive attack.

Acknowledgements

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References

[1] J.F. Wang, A.R. Sethuraman, L.M. CooK, R.C. Kistler, G.P. Schwartz, Semicond. Int. 18 (1995) 117.

[2] K. Kikuta, in: Proceedings of the International Electron Devices Meeting, A4-3-P, 1996, p. 161.
[3] S. Kordic, C.A.H. Mutsaers, H. Lifka, M.N. Webster, in: Proceedings of the IEEE IITC, 1998, p. 70.
[4] R.V. Joshi, IEEE Electro Dev. Lett. 15 (3) (1993) 129.
[5] C.W. Kaanta, S.G. Bombardier, W.J. Cote, W.R. Hill, G. Kerszykoweki, J.E. Cronin, et al., in: Proceedings of the Eighth International VLSI Multilevel Interconnection Conference, 1881, p. 155.
[6] M.A. Fury, D.L. Scherber, M.A. Stell, MRS Bull. (1995) 161.
[7] C.G. Kallingal, D.J. Duquette, S.P. Murarka, J. Electrochem. Soc. 145 (1998) 2074.
[8] J.M. Steigerwald, S.P. Murarka, R.J. Gutmann, D.J. Duqutte, Mater. Chem. Phys. 41 (1995) 217.
[9] P. Wrschka, J. Hernandez, Y. Hsu, T.S. Kuan, G.S. Oehrlein, H.J. Sun, D.A. Hansen, J. King, M.A. Fury, J. Electrochem. Soc. 146 (1999) 2689.
[10] P. Singer, Semicond. Int. 21 (1998) 46.
[11] L. Peters, Semicond. Int. 21 (1998) 83.
[12] R. Iggulden, et al., Solid State Technol. (1998) 37.
[13] C.C. Yu, T.T. Doan, A.E. Laulusa, US Patent 5 209 816 (1993).
[14] D.A. Jones, Principles and Prevention of Corrosion, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ, 1996, pp. 94, 177, 183.
[15] E.A. Kneer, C. Raghunath, V. Mathew, S. Raghavan, J. Electrochem. Soc. 144 (1997) 3041.
[16] R. Carpio, J. Farkas, R. Jairath, Thin Solid Films 266 (1995) 238.
[17] J.A. Franklin, Atlas of Electrochemical Equilibria, 2nd ed., Pergamon Press, Oxford, 1974, pp. 158, 213.
[18] D. Zeidler, Z. Stavreva, M. Plotner, K. Drescher, Microelectron. Eng. 33 (1997) 259.
[19] J.M. Steigerwald, D.J. Duqutte, S.P. Murarka, R.J. Gutmann, J. Electrochem. Soc. 142 (1995) 2379.
[20] D.R. Evans, Electrochem. Soc. Proc. 96–22 (1997) 70.