Ti CMP process for better topography control in advanced 3D packaging

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INTRODUCTION
Multi-layer stacking technology in 3D packaging has advanced rapidly, enhancing the device’s performance, reducing power consumption and overcoming the limitations in reducing the size of the structures. The multiple layers of chips in 3D structures are interconnected to each other by using through silicon vias (TSVs) [1, 2]. As the advanced package utilizes porous ultra-low K (ULK) dielectric, the Ti-based barrier layer is preferred due to its better resistance to the moisture associated with the dielectric layer [3]. Controlling topography in reducing surface defects (i.e., dishing and erosion) during the oxide stop buffing CMP step is critical for Cu-to-Cu hybrid bonding. The surface defects after the CMP process lead to poor Cu-to-Cu hybrid bonding in 3D structures, and thereby it is requisite to understand the Ti CMP mechanism for better topography control in advanced 3D packaging.

BACKGROUND
The behavior of oxidation and dissolution of Ti during the CMP process is the key step in understanding the mechanism of Ti CMP. Ti is resistant to corrosion in most corrosive environments due to its protective oxide layer on the surface. However, it undergoes corrosion in alkaline hydrogen peroxide solutions due to the less protective film on the surface. The dissolution mechanism of Ti in alkaline hydrogen peroxide solutions has been studied in various literature [4]; however, no studies are available on the Ti CMP mechanism for better topography control in advanced 3D packaging. In alkaline hydrogen peroxide conditions, titanium surfaces are covered with a softer film that can be easily removed during the CMP process. The selectivity in removing Ti over Cu and TEOS is critical in controlling the dishing and erosion during the CMP process. In the current study, the dissolution and removal of Ti at different pH and H₂O₂ concentrations were studied, and the dissolution mechanism was supported with electrochemical analysis at different pHs and H₂O₂ concentrations.

EXPERIMENTAL
The removal rate of Ti was estimated from the CMP experiments, carried out using a Poli-500 polisher (GnP polisher-500, Korea) with a Visionpad 3100 (Dupont, US). Ti wafers of film thickness 4000 nm received from Samsung, South Korea, were cut into coupons of size (4×4 cm²) and were used for all the polishing and static etch rate experiments. The CMP was performed with a slurry containing 3 wt.% colloidal silica abrasives (AceNanocam, Korea) and various concentrations of hydrogen peroxide (0-2 wt.%). The polishing experiments were performed for 1 min, and the slurry flow rate was maintained at 100 mL/min. The applied downforce was 1.5 psi with rotation speeds of the platen, and the head was maintained at 93 and 78 rpm, respectively. The static etch rate (SER) was measured at various conditions similar to the CMP experiments without silica particles. The removal rate and etch rate of titanium were obtained by measuring the sheet resistance of the Ti surface using a 4-point probe instrument CMT-5000 (AIT, Korea). Potentiodynamic polarization of Ti at different pH with various concentrations of H₂O₂ was performed to study the oxidation and dissolution of Ti. A conventional three-electrode setup connected to the Versa STAT 3 (Princeton Applied Research, US) potentiostat was used to perform the electrochemical experiments. Ti coupons of size 2×2 cm were used as the working electrode. Ag/AgCl in saturated KCl and platinum mesh were used as the reference and counter electrodes, respectively. Before each experiment, Ti samples were pretreated by dipping them in DHF for 1 min to remove the native oxide from the surface. Potentiodynamic polarization was performed over a potential range of −250 to 500 mV above and below OCP at a rate of 1 mV/s. The corrosion potential (Ecorr) and the corrosion current density values (icorr) were calculated using Tafel extrapolation in VersaStudio software.
Fig. 1 Experimental procedure for (a) etching, (b) CMP, and (c) electrochemical analysis of Ti coupons under various conditions.

**DISCUSSION**

Fig. 2 shows the SER of titanium at different pH values and H₂O₂ concentrations. In the absence of H₂O₂, Ti showed almost zero SER with no change in thickness at all tested pH values. Based on the Eh-pH diagram for the Ti-H₂O system, titanium is passivated under alkaline conditions with Ti₂O₃ or TiO₂ [4]. However, Ti dissolution becomes significant with the addition of H₂O₂ for pH 6 to 10. Below pH 6, etch rate of Ti was negligible at all concentrations of H₂O₂ studied. This indicates the presence of a stable passive oxide layer on the surface of Ti. For a given concentration of H₂O₂, the SER of Ti increases with the pH of the solution. Similarly, the SER increases with the concentration of H₂O₂ at a constant pH between 6 to 10. The highest SER of 22 nm min⁻¹ was observed at pH 10 with 2 wt.% of H₂O₂. This indicates the significantly fast dissolution of the oxide formed on the surface of Ti in the alkaline condition at high H₂O₂ concentration. The potentiodynamic polarization curves of Ti at different pH at 2 wt.% H₂O₂ are shown in Fig. 3. Polarization data indicates that the open circuit potential (OCP) of Ti decreases with the increase in pH of the solution for the cases with and without H₂O₂. The polarization current increases significantly with the addition of H₂O₂ under all pH conditions, indicating enhanced electrochemical reactions on the surface of Ti. The corrosion potential (E_{corr}) and corrosion current (i_{corr}), estimated from the Tafel extrapolation, are given in Table 1. The i_{corr} value increases at a lower rate with the increase in pH from 2 to 10. The highest value of i_{corr} was observed at pH 10 with 2 wt.% of H₂O₂, showing a significant dissolution of Ti. At pH 10, the addition of 2 wt.% of H₂O₂ decreases the OCP value and increases the i_{corr} value, signifying the enhanced Ti dissolution with chemically active surface oxide or peroxide. Thus, it can be predicted that in the presence of hydrogen peroxide, a more stable oxide film is formed at the acidic pH, and a less stable oxide is formed at
the alkaline pH. The electrochemical results are compatible with the SER data, where both SER and $i_{\text{corr}}$ values increase with pH and H$_2$O$_2$.

Fig. 2 Static etch rate of Ti at different pH values and H$_2$O$_2$ concentrations

Fig. 3 Potentiodynamic polarization plots for Ti at different pH values with and without 2 wt.% H$_2$O$_2$

Table 1 Tafel extrapolated values of $E_{\text{corr}}$ and $i_{\text{corr}}$ corresponding to the Ti at different pH values with and without 2 wt% H$_2$O$_2$

<table>
<thead>
<tr>
<th>pH</th>
<th>$E_{\text{corr}}$ (mV vs Ag, AgCl)</th>
<th>$i_{\text{corr}}$ (µA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt% H$_2$O$_2$</td>
<td>2.0 wt% H$_2$O$_2$</td>
</tr>
<tr>
<td>2</td>
<td>-158 ± 4</td>
<td>29 ± 2</td>
</tr>
<tr>
<td>6</td>
<td>-305 ± 5</td>
<td>194 ± 2</td>
</tr>
<tr>
<td>10</td>
<td>-471 ± 2</td>
<td>590 ± 6</td>
</tr>
</tbody>
</table>

The titanium etching mechanism in the presence of H$_2$O$_2$ occurs via continuous formation and dissolution of the Ti oxide by H$_2$O$_2$. The dissolution of Ti oxides occurs in multiple steps, as shown in Eqns. 1-3 [4].
Titanium in alkaline pH forms protective oxide and results in a very low dissolution rate (Eqn. 1). However, dissociation of peroxide in alkaline solutions forms the perhydroxyl ion (OOH\(^-\)), which reacts with Ti to form a highly soluble peroxide complex on the surface, Ti(OH)\(_2\)O (Eqn. 2). At sufficiently high pH and H\(_2\)O\(_2\) concentrations (high OOH\(^-\)), reactions between the adsorbed complex and OOH\(^-\) occurs to form the soluble Ti species. The entire mechanism of Ti oxidation and dissolution in alkaline peroxide solution by the complexation with H\(_2\)O\(_2\) is shown in Fig. 4 [5].

\[
\begin{align*}
\text{Ti} + (x-2)\cdot \text{H}_2\text{O} + 4\text{OH}^- & \rightarrow \text{TiO}_2\cdot x(\text{H}_2\text{O}) + 4e^- \quad [1] \\
\text{TiO}_2\cdot x(\text{H}_2\text{O}) + \text{OOH}^- & \rightarrow (\text{Ti}[\text{OH}]_2\text{O}_2)_{\text{ads}} + (x-1)\cdot \text{H}_2\text{O} + \text{OH}^- \quad [2] \\
(\text{Ti}[\text{OH}]_2\text{O}_2)_{\text{ads}} + \text{OOH}^- & \rightarrow \text{HTiO}_3^- + \text{H}_2\text{O} + \text{O}_2 \quad [3]
\end{align*}
\]

Fig. 4 Illustration of the Ti etching mechanism by H\(_2\)O\(_2\)

The titanium RR at different pH and H\(_2\)O\(_2\) concentrations are shown in Fig. 5a. The RR of Ti without H\(_2\)O\(_2\) was minimum at all pH conditions compared to the conditions with H\(_2\)O\(_2\). This is mainly because of the thin protective oxide layer formation of TiO\(_3\) or TiO\(_2\) without H\(_2\)O\(_2\). At high concentrations of H\(_2\)O\(_2\) (>0.5 wt%), the RR increases gradually with an increase in the pH of the solution. The high removal rate observed in alkaline hydrogen peroxide solution is due to the formation of Ti(OH)\(_2\)O\(_2\) on the surface, which can be removed easily. The maximum RR of ~100 nm min\(^{-1}\) was observed at pH 10 with 2 wt.% H\(_2\)O\(_2\). The high SER of Ti, comparable to the RR, at pH 10 with 2 wt.% H\(_2\)O\(_2\) indicates that chemical etching is significant in alkaline hydrogen peroxide solutions. The mechanism of Ti CMP in alkaline hydrogen peroxide solution is shown in Fig. 5b. The thick oxide formed on the Ti surface, Ti(OH)\(_2\)O\(_2\), is easily removed during the abrasion of colloidal silica and exposes fresh Ti surface, which reacts with OOH\(^-\) ions and again produces Ti(OH)\(_2\)O\(_2\) layer on the surface. The cyclic formation and removal of Ti(OH)\(_2\)O\(_2\) during Ti CMP in alkaline hydrogen peroxide resulted in the high removal rate of Ti.

Fig. 5 (a) RR of Ti at different pH values and H\(_2\)O\(_2\) concentration and (b) the mechanism of Ti CMP in the alkaline hydrogen peroxide solution

CONCLUSIONS

This study discussed the Ti CMP mechanism, which is critical in the topographic control for Cu-to-Cu bonding in 3D packaging. The SER of Ti in alkaline hydrogen peroxide conditions shows a high etch rate due to the formation of the easily dissolving layer. The \(i_{\text{corr}}\) values estimated from the potentiodynamic polarization data were consistent with the SER data and showed significantly high \(i_{\text{corr}}\) in alkaline hydrogen peroxide solution. The results indicate that Ti CMP in alkaline hydrogen peroxide is controlled by combined chemical dissolution and mechanical removal mechanism. Hence, this condition is suitable for the barrier CMP process for fine topography control in advanced 3D packaging.
REFERENCE


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