

Application of Potential-pH Diagram and Potentiodynamic Polarization of Tungsten

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The oxidizer-induced corrosion state and microstructure of surface passive metal-oxide layer greatly influenced on the removal rate of tungsten film according to the slurry chemical composition of different mixed oxidizers. In this paper, the actual polishing mechanism and pH-potential equilibrium diagram obtained from potentiodynamic polarization curve were electrochemically compared. An electrochemical corrosion effect implies that slurries with the highest removal rate (RR) have the high dissolution rate.

Keywords : Chemical mechanical polishing (CMP), Potentiodynamic polarization, Pourbaix

1. INTRODUCTION

Tungsten (W) has been widely used as a plug for the multi-level interconnection structures. Chemical mechanical polishing (CMP) process has been accepted as the planarization technique for fabrication of tungsten plug [1]. The CMP process has to provide a high removal rate (RR), good global and local planarity, high selectivity, and a clean post-CMP surface[2,3]. The slurries used in the W-CMP process typically contain a strong oxidizer and are employed at acidic pH[3]. Thus, it is important to understand the effect of oxidizer on passive tungsten-oxide layer in order to obtain a higher RR during the W-CMP process. Typically, the alumina (Al₂O₃)-based W-slurry uses H₂O₂ as an oxidizer[4]. A suitable oxidizer should be chosen, because the oxidizer had a leading role on RR of tungsten film. In this study, new mixed oxidizers were proposed with a different mixing ratio by adding KIO₃ and Fe(NO₃)₃ into the best stable H₂O₂ for the excellent corrosion effect. The electrochemical measurements for slurry compositions were also investigated with the mixed oxidizers in order to estimate the correlations between the kinetics of passive metal-oxide and the RR of tungsten film.

2. EXPERIMENTAL DETAILS

Blanket wafers of W/tetra-ethyl ortho-silicate (TEOS)/

Si structure were prepared and Al₂O₃-based W-slurry (RODEL, MSW 2000A) was used as starting slurry. H₂O₂, Fe(NO₃)₃, and KIO₃ were adopted as a mixed oxidizer. Table 1 summarizes the mixing ratio of oxidizer additive. The CMP experiments were performed using a G&P POLI-380 CMP polisher and the polishing pad was a double pad with stack-type IC-1300/Suba-IV from RODEL Company. The process conditions of polisher are as follows; the rotation speed of table and head were both set to 70 rpm, and head pressure was set to 60 gf/cm². Also, polishing time was fixed as 60 s. To prevent the aging effect and precipitation of mixed slurry, the slurry was dispersed using a stirrer before polishing. For post-CMP cleaning, we cleaned by using ultrasonic for 4 minutes in diluted HF solution, after rinsing in ammonium hydroxide (NH₄OH) solution of 2 % for 20 s. The potentiodynamic polarization test was performed using a potentiostat CMS-100 model manufactured by Gamry Company. A carbon rod and a saturated calomel electrode (SCE) were used for the counter and reference electrodes, respectively. The electrode rod was used to investigate the tungsten dissolution behavior under hydrodynamic conditions. During the potentiodynamic scans, the working electrode potential was varied with a scanning rate of 1 mV/sec from -500 mV/SCE to +1,000 mV/SCE in the positive direction, in order to measure the electrochemical corrosion behavior such as corrosion potential or corrosion current density.

Table 1. Solution of mixed oxidizers.

No.	Mixed Oxidizer			
#1	H ₂ O ₂	5 wt%	+ KIO ₃	1 wt%
#2	H ₂ O ₂	5 wt%	+ KIO ₃	3 wt%
#3	H ₂ O ₂	5 wt%	+ KIO ₃	5 wt%
#4	H ₂ O ₂	5 wt%	+ Fe(NO ₃) ₃	1 wt%
#5	H ₂ O ₂	5 wt%	+ Fe(NO ₃) ₃	3 wt%
#6	H ₂ O ₂	5 wt%	+ Fe(NO ₃) ₃	5 wt%

3. RESULTS AND DISCUSSION

The RRs of tungsten film as a function of H₂O₂ concentration as an oxidizer were reported[5,6]. In case the contents of H₂O₂ is below 5 wt%, W-CMP is being controlled only by the low oxidation rate of tungsten itself and the mechanical force of abrasives, because the passive layer of WO₃ fails to be formed completely and it forms an unstable WO_x film. However, in case H₂O₂ over 5 wt% is added, because the formation of WO₃ as a passive layer and chemical etching due to excessive oxidizer were simultaneously performed, it shows a non-linear RR. Especially, in case of 5 wt% adding, the removal mechanism revealed a very superior ability, because the both chemical and mechanical action due to the formation of sufficient WO₃ passive layers almost concurrently occurred. Figure 1 shows the corrosion potentials determined by the intersections of cathodic and anodic curves obtained from potentiodynamic polarization test with pH change. A remarkable difference is observed in the electrochemical behavior.

The mixture of KIO₃ with 5 wt% H₂O₂ revealed a decrease of corrosion potential with an increase of pH as represented in Fig. 1. The mixture of Fe(NO₃)₃ with 5 wt%

H₂O₂ displayed an increase of corrosion potential with a decrease of pH as shown in Fig. 1. The passive layer of WO₃ was formed in the Fe(NO₃)₃ additive slurry judging from a potential-pH equilibrium diagram for the W-H₂O₂ system[7]. WO₃ is softer than tungsten and therefore abrades more easily[8]. The Fe(NO₃)₃-added slurry removed and passivated the surface of tungsten simultaneously and repetitively, which means that the formation of WO₃ on the surface prevented further oxidation of the tungsten substrate and then the mechanical force of abrasives in the slurry removed the surface exposing the underlying tungsten to the corrosive effects of the slurry[8]. However, according to a potential-pH equilibrium diagram for the W-H₂O₂ system[7], the corrosion product of WO₄²⁻ was formed in the KIO₃-added slurry. WO₃ passive layer was not established in this slurry and therefore the corrosive tungsten surface of WO₄²⁻ was removed by only the chemical etching.

Figure 2 shows the RRs and the corrosion current densities determined by the intersections of cathodic and anodic curves of polarization test using various mixed oxidizers by additions of KIO₃ and Fe(NO₃)₃ to 5 wt% H₂O₂ oxidizer which has the most stable corrosion effect as the above-mentioned oxidizer test result. As the Fe(NO₃)₃ was added to the H₂O₂ oxidizer of 5 wt%, the corrosion current density was rapidly increased, whereas the KIO₃ showed a slightly increased tendency. The increase of corrosion current density implies that oxidizer can significantly increase a corrosion rate. It is well known that the high corrosion rate directly relates to the fast dissolution rate and the high RR. In terms of RR analysis, high RR was seen in all the cases that Fe(NO₃)₃ was added in H₂O₂ oxidizer of 5 wt%. On the other hand, the polishing action did not happen in all the cases that

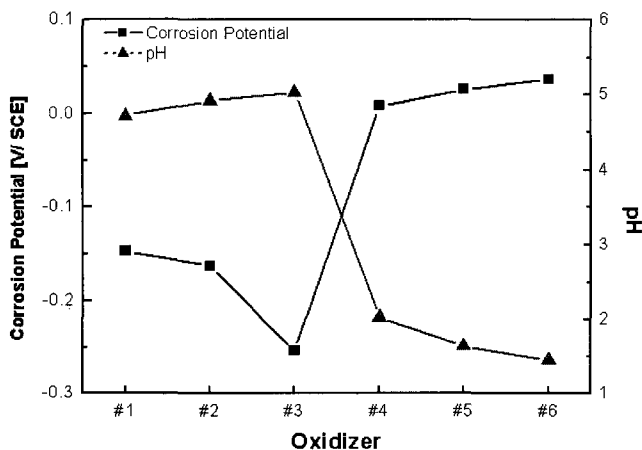


Fig. 1. Corrosion Potential and pH of tungsten film with the mixed oxidizers as listed in Table 1.

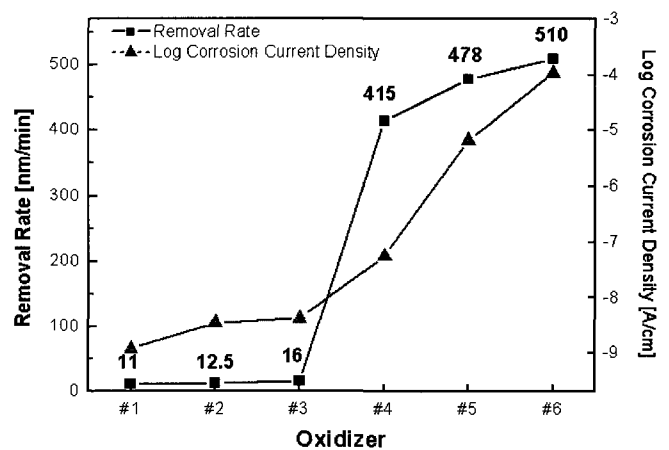
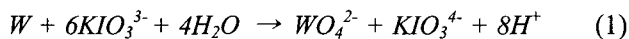


Fig. 2. Corrosion current density and RR of W-film with the mixed oxidizers as listed in Table 1.

KIO₃ was added in H₂O₂ oxidizer of 5 wt%. The tendency of RR was exactly alike that of the corrosion current density as shown in Fig. 2. This means that the control of oxidizer additive amounts is very crucial. Also, it could be seen that the role of oxidizer is very important during W-CMP process.

Figure 3 shows the Pourbaix diagram for tungsten[7]. Tungsten is passivated at low pH and dissolved above pH=5, whereas it is stable in all pH ranges under -1.3 V/SCE[7]. The experimental potentials-pH data obtained from the mixed oxidizers listed in Table 1 were directly marked in this diagram adapted from reference[7]. KIO₃-mixed slurry corrodes the tungsten surface as shown in Pourbaix diagram with the marked experimental data. In the KIO₃-mixed slurry at pH above 4, dissolution of tungsten occurs according to:



The above reactions indicates that WO₃ passive layer is not established in this slurry and therefore the corrosion product of WO₄²⁻ was removed by only the chemical dissolution, which is in good agreement with the potential-pH diagram for the W-H₂O system[7]. According to Kaufman's mechanisms[1], the polishing mechanism of W-CMP process has been reported as the repeated process of passive metal-oxide formation by oxidizer and abrasion action by slurry abrasives. WO₃ was formed on tungsten surface at low pH in Fe(NO₃)₃-mixed slurry as shown by the marked experimental data in Fig. 3. In other words, Fe(NO₃)₃ oxidizes W surface via following chemical reaction:

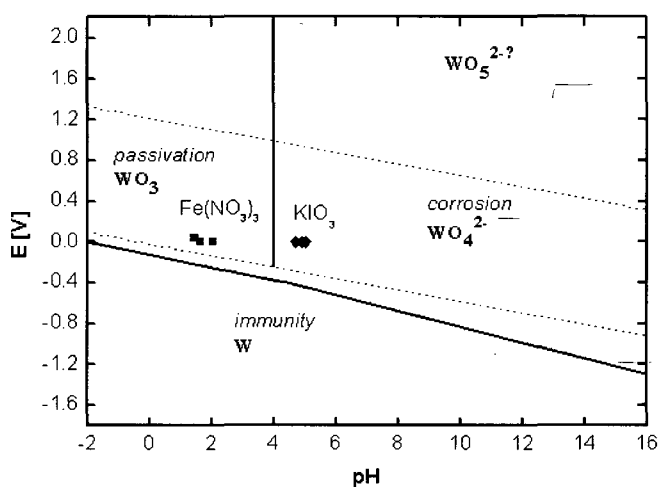
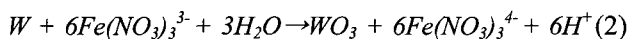


Fig. 3. Pourbaix diagram adapted from reference[7]. Our potential-pH data marked in Figure using different symbol.

Once WO₃ establishes, it prevents the further oxidation and dissolution of the underlying tungsten by the slurry. Then, the mechanical action of the alumina abrasive particles in the mixed slurry not only removes the surface layer but also exposes and re-passivates the underlying tungsten surface to the formation of WO₃ spontaneously[8].

4. CONCLUSION

In practical CMP experiments, we confirmed that fast and effective formation of surface oxide layer was the key factors for achieving the high RR and better W-CMP performance. According to the electrochemical and surface morphology analysis, the oxidizer-induced corrosion state and microstructure of surface passive oxide layer were greatly influenced by the slurry chemical composition of different mixed oxidizers. For the case of Fe(NO₃)₃-mixed slurry, the passive tungsten-oxide layer was formed in contrast to KIO₃ showing predominant corrosion. The control of oxidizer additive amounts is very crucial.

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