Scavenger with Protonated Phosphite Ions for Incredible Nanoscale ZrO$_2$-Ablasive Dispersant Stability Enhancement and Related Tungsten-Film Surface Chemical–Mechanical Planarization

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Abstract: For scaling-down advanced nanoscale semiconductor devices, tungsten (W)-film surface chemical mechanical planarization (CMP) has rapidly evolved to increase the W-film surface polishing rate via Fenton-reaction acceleration and enhance nanoscale-ablative (i.e., ZrO$_2$) dispersant stability in the CMP slurry without a decrease in the W-film surface polishing rate. A scavenger with protonate-phosphite ions was designed to suppress the time-dependent Fenton reaction. The ZrO$_2$ dispersant stability (i.e., lower H$_2$O$_2$ decomposition rate and longer H$_2$O$_2$ pot lifetime) linearly and significantly increased with scavenger concentration. However, the corrosion magnitude on the W-film surface during CMP increased significantly with scavenger concentration. By adding a scavenger to the CMP slurry, the reaction reduction via Fenton-reaction suppression in the CMP slurry and the corrosion enhancement on the W-film surface during CMP performed that the W-film surface polishing rate decreased linearly and notably with increasing scavenger concentration via a chemical-dominant CMP mechanism. Otherwise, the SiO$_2$-film surface polishing rate peaked at a specific scavenger concentration via a chemical and mechanical-dominant CMP mechanism. The addition of a corrosion inhibitor with a protonate-amine functional group to the W-film surface CMP slurry completely suppressed the corrosion generation on the W-film surface during CMP without a decrease in the W- and SiO$_2$-film surface polishing rate.

Keywords: tungsten; chemical-mechanical-planarization; scavenger; protonated phosphite-ion; Fenton reaction; corrosion

1. Introduction

Recently, nanoscale semiconductor devices have been rapidly scaling down to achieve faster switching, lower power consumption, and lower bit cost; that is, less than a 14 nm design rule for dynamic random-access memory (DRAM), higher than 128-floor memory-cells for three-dimensional (3D) NAND flash memory, and less than 5 nm design rule for application processors [1–5]. For fabricating advanced nanoscale semiconductor devices, tungsten (W)-film surface chemical mechanical planarization (CMP) utilized for W buried-gate, W wiring, and plugs has evolved toward a critical CMP performance, such as a higher W-film surface polishing rate, free of dishing, and erosion at a smaller W line width and a higher aspect ratio at the remaining W-film in plugs after CMP [6–9]. The W-film surface CMP is principally conducted by the Fenton reaction between the ferric–ionic catalyst and...
oxidant (i.e., hydrogen peroxide: \( \text{H}_2\text{O}_2 \)) \[10,11\], which produces significantly dissolved \( \text{O}_2 \) and radicals (i.e., \( \text{OH}^\cdot \), \( \text{HO}_2^\cdot \) and \( \text{O}_2^{-} \)) and chemically oxidizes the W film surface by forming a nanoscale thick oxide layer (i.e., \( \text{WO}_3 \)). Thus, the W-film surface CMP is conducted by mechanical rubbing between nanoscale abrasives (i.e., colloidal silica or \( \text{ZrO}_2 \)) and a nanoscale thick \( \text{WO}_3 \) layer on the W-film surface. In particular, the produced radicals accelerate the Fenton reaction, which is called a cycling chemical reaction process \[12,13\]. Recently, several studies on W-film surface CMP have been reported, i.e., a design for a new ferric-ionic catalyst for enhancing the W-film surface polishing rate \[11,14\], a design for a selectivity agent for increasing the polishing rate selectivity between W- and \( \text{SiO}_2 \)-film surface \[15\], and a design for the scavenger for improving the abrasive stability in CMP slurry \[10\]. In particular, to enhance the W-film polishing rate during CMP, the Fenton reaction between a ferric-ionic catalyst and oxidant (i.e., \( \text{H}_2\text{O}_2 \)) was essentially accelerated by designing ferric-ionic catalysts properly and increasing the oxidant concentration, which is a chemical-dominant CMP mechanism. However, the acceleration of the Fenton reaction in the W-film surface CMP slurry can induce a remarkable degradation of the nanoscale abrasive dispersant stability in the CMP slurry, resulting in fast sedimentation of the nanoscale abrasives in the CMP slurry during CMP \[10\].

Thus, to enhance the abrasive dispersant stability in the CMP slurry, a scavenger with carboxyl functional groups (i.e., trilithium citrate tetrahydrate: TCT–Li) for suppressing the Fenton reaction was proposed, which showed a \( \text{H}_2\text{O}_2 \) pot lifetime of less than 50 h. Note that the \( \text{H}_2\text{O}_2 \) pot lifetime is defined by the rapid increase in the secondary abrasive size after the oxidant (i.e., \( \text{H}_2\text{O}_2 \)) was mixed with the W-film surface CMP slurry \[10\]. In addition, the achievement of a \( \text{H}_2\text{O}_2 \) pot lifetime longer than 7 days is vitally necessary for massive semiconductor fabrication. As a solution to further enhance the \( \text{H}_2\text{O}_2 \) pot lifetime, in this study, a scavenger with protonated phosphate ions was designed for a W-film surface CMP slurry. First, the effect of the nanoscale \( \text{ZrO}_2 \)-abrasive dispersant stability on the scavenger type and concentration was examined, where two scavengers with protonated phosphate ions (i.e., etidronic acid: EA and phosphorous acid: PA) and two scavengers with protonated phosphate ions (i.e., monoammonium phosphate: MAP, monopotassium phosphate: MPP) were tested. Note that nanoscale \( \text{ZrO}_2 \) abrasives were used for a W-film surface CMP slurry, since they could achieve a dishing-free W-film surface CMP performance \[11\]. The improvement in the magnitude of the \( \text{ZrO}_2 \) abrasives in the slurry was estimated by the \( \text{H}_2\text{O}_2 \) decomposition rate and \( \text{H}_2\text{O}_2 \) pot lifetime. Thus, the dependence of the \( \text{H}_2\text{O}_2 \) decomposition rate on the scavenger type and concentration in the W-film surface CMP slurry was investigated. In particular, the Fenton reaction, depending on the scavenger type and concentration, was analyzed by the chemical reaction equations. In addition, the dependencies of the W- and \( \text{SiO}_2 \)-film surface polishing rate on the scavenger type and concentration were estimated. Moreover, the dependence of the W-film surface corrosion magnitude (i.e., static etch rate and corrosion current) on the scavenger concentration were observed to characterize the chemical-dominant CMP performance. Finally, the CMP mechanism (i.e., chemical-dominant CMP or mechanical-dominant CMP) of the W- and \( \text{SiO}_2 \)-film surface, depending on the scavenger concentration, was proved by chemical composition analysis of the W- and \( \text{SiO}_2 \)-film surfaces using X-ray photoelectron spectroscopy (XPS) and calculating the electrostatic force between the \( \text{ZrO}_2 \) abrasive and the zeta potential of W- and \( \text{SiO}_2 \)-film surfaces.

2. Materials and Methods

2.1. Materials

A 300 nm-thick \( \text{SiO}_2 \)-film was deposited on a 12 inch-diameter Si wafer by chemical vapor deposition. The W-film surface CMP slurries were composed of colloidal monoclinic crystallized \( \text{ZrO}_2 \) abrasives with a 40 nm primary abrasive size, a catalyst (i.e., \( \text{Fe(NO}_3\text{)}_3 \)), a phosphate-based scavenger (i.e., etidronic acid: EA or phosphorous acid: PA) or a phosphate-based scavenger (i.e., monopotassium phosphate: MPP or monoammonium phosphate: MAP), a corrosion inhibitor (i.e., asparagine), a pH titrant (i.e., \( \text{HNO}_3 \)),...
an oxidant (i.e., H$_2$O$_2$), and deionized water (DIW). The ZrO$_2$ abrasives (1 wt%) were dispersed using a polycarboxylic acid-type dispersant through a ball-mill process in DIW. Phosphite- or phosphate-based scavengers (0–0.25 wt%) were added to the W-film surface CMP slurries. Ferric nitrate (i.e., Fe(NO$_3$)$_3$) of 0.15 wt% was used as a Fenton reaction catalyst to increase the W-film surface polishing rate. Afterward, the slurries were titrated to pH 2 using a pH titrant (i.e., HNO$_3$). The slurry and DIW ratios were diluted to 1:1, and then 1.5 wt% of H$_2$O$_2$ was added to the W-film surface CMP slurries.

2.2. CMP Conditions

To estimate the CMP performance of the slurries, a 12 inch diameter wafer with a vertical structure of Si substrate, 100 nm thick SiO$_2$ film, 100 nm thick TiN film and 250 nm thick W-film, and a 12 inch diameter wafer with a vertical structure of Si substrate, a 450 nm thick SiO$_2$ film were used. The wafers were polished using a polishing machine (AP-300, CTS Co., Inc., Cheongju, Korea) and a CMP pad (IC 1000/Suba IV, Dupont Co., Inc., Wilmington, DE, USA). The W-film surface slurries were diluted with DIW to a ratio of 1:1. After that, H$_2$O$_2$ was added to the CMP slurry, and the mixed slurry was stirred at 300 rpm for 1 h in the CMP supply tank. The mixed slurries with a slurry flow rate of 200 mL/min were dropped from the supply tank over the CMP pad during CMP. The polishing table rotation speed and wafer carrier rotation speed were 87 and 93 rpm, respectively, the polishing head pressure was 3 psi, and the polishing time was 1 min.

2.3. Measurement Equipment

The polishing rate of the SiO$_2$-film surface was calculated by measuring the SiO$_2$-film thickness before and after CMP using an ellipsometer (V-VASE, J.A. Woollam Co., Inc., Lincoln, NE, USA). In addition, the W-film surface polishing rate was estimated by measuring the difference in sheet resistance before and after CMP using a four-point probe (CMT-SR5000, AIT Co., Inc., Suwon, Korea). After dipping the W film into W-film CMP slurries at 65 °C for 3 min, the surface morphology of the W-film surfaces was observed using a scanning electron microscope (SEM, S-4800, Hitachi Co., Inc., Tokyo, Japan) at an accelerating voltage of 5 kV. A potentiostat (CHI750, CH Instruments Co., Inc., Austin, TX, USA) was used to measure the corrosion potential and current of the W-film surface after dipping the W film into W-film CMP slurries at 65 °C for 5 min. The chemical composition of the W-film surface after CMP was analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha+, Thermo Fisher Scientific Co., Inc., Waltham, MA, USA) using an Al Kα source (1486.6 eV) at 12 keV and 6 mA. The secondary abrasive size was measured using a laser-scattering particle size distribution analyzer (LA-960S, HORIBA Scientific Co., Inc., Kyoto, Japan) to estimate the ZrO$_2$ abrasive dispersant stability in the W-film CMP slurry. The zeta potentials of the ZrO$_2$ abrasives, WO$_3$ particles, and SiO$_2$ particles were measured with a particle analyzer using the electrophoretic light-scattering method (ELSZ2+, Otsuka Electronics Co., Inc., Osaka, Japan).

3. Results and Discussion

3.1. Abrasive Dispersant Stability of W-Film Surface CMP Slurry Depending on Phosphite or Phosphate-Based Scavenger Type and Concentration

The Fenton reaction between ferric–ionic catalyst (i.e., Fe(NO$_3$)$_3$) and oxidant (i.e., H$_2$O$_2$) including a phosphate-based scavenger (i.e., C$_2$H$_8$O$_7$P$_2$: EA) can be described by Equations (1)–(11).

\[
\text{Fe(NO}_3\text{)}_3 \rightarrow \text{Fe}^{3+} + 3(\text{NO}_3^-) \quad (1)
\]
\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{FeOOH}^{2+} + \text{H}^+ \quad (2)
\]
\[
\text{FeOOH}^{2+} \rightarrow \text{Fe}^{2+} + \text{HO}_2^- \quad (3)
\]
\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \quad (4)
\]
\[
\text{OH}^* + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (5)
\]
HO$_2^•$ → H$^+$ + O$_2$•$^-$  
(6)

O$_2$•$^-$ + Fe$^{3+}$ → O$_2$ + Fe$^{2+}$  
(7)

C$_2$H$_8$O$_7$P$_2$ → 2H$^+$ + (C$_2$H$_6$O$_7$P$_2$)$^{2-}$  
(8)

4OH$^•$ + 2(C$_2$H$_6$O$_7$P$_2$)$^{2-}$ → 4H$_2$O + (C$_2$H$_7$O$_7$P$_2$)-(C$_2$H$_7$O$_7$P$_2$)  
(9)

4HO$_2^•$ + 2(C$_2$H$_6$O$_7$P$_2$)$^{2-}$ → 2O$_2$ + 4H$_2$O + (C$_2$H$_7$O$_7$P$_2$)-(C$_2$H$_7$O$_7$P$_2$)  
(10)

2O$_2$•$^-$ + 4(C$_2$H$_6$O$_7$P$_2$)$^{2-}$ → 4H$_2$O + 2[(C$_2$H$_7$O$_7$P$_2$)-(C$_2$H$_7$O$_7$P$_2$)]  
(11)

6OH$^•$ + W → WO$_3$ + 3H$_2$O  
(12)

W + O$_2$ → WO$_2$  
(13)

2WO$_2$ + O$_2$ → 2WO$_3$  
(14)

2WO$_3$ + 2(C$_2$H$_6$O$_7$P$_2$)$^{2-}$ + 3O$_2$ → 2(WO$_4^{2-}$) + 4CO$_2$ + 4H$_2$O + 2H$_2$PO$_3^-$  
(15)

The Fenton reaction produces reactive radicals such as OH$^•$, HO$_2^•$, and O$_2$•$^-$ in the W-film surface CMP slurry, and the produced OH$^•$, HO$_2^•$, and O$_2$•$^-$ significantly accelerated the decomposition of H$_2$O$_2$ into the dissolved O$_2$ in the slurry; this process is called a cycling chemical reaction process, as shown in Equations (1)–(7). As a result, the W-film surface was chemically oxidized; that is, the formation of WO$_3$ on the W-film surface, as shown in Equations (12)–(14). The W-film surface CMP is principally conducted by the formation of WO$_3$ on the W-film surface, followed by mechanical rubbing between the ZrO$_2$ abrasive and the nanoscale thick WO$_3$ layer. However, the produced OH$^•$, HO$_2^•$, and O$_2$•$^-$ could chemically react with the dispersant polymer (i.e., polycarboxylic acid-type polymer) coated on ZrO$_2$ abrasives, which significantly degrades the ZrO$_2$ abrasive dispersant stability in the slurry [16,17]. The addition of a phosphite-based scavenger (i.e., etidronic acid (C$_2$H$_6$O$_7$P$_2$): EA) to the W-film surface CMP slurry significantly suppressed the Fenton reaction via a chemical reaction between the negatively charged C$_2$H$_6$O$_7$P$_2^{2-}$ and radicals (i.e., OH$^•$, HO$_2^•$ and O$_2$•$^-$), producing H$_2$O$_2$ and neutral C$_2$H$_8$O$_7$P$_2$, as shown in Equations (8)–(11). As a result, the amount of OH$^•$, HO$_2^•$ and O$_2$•$^-$ in the slurry could be reduced significantly, improving the stability of the ZrO$_2$ abrasive dispersant in the slurry. Thus, in order to estimate the magnitude of improvement of the ZrO$_2$ abrasive dispersant stability in the W-film surface CMP slurry including a scavenger, the dependence of the H$_2$O$_2$ decomposition rate on a phosphite (i.e., EA and PA) or a phosphate (i.e., MPP and MAP)-based-scavenger type and concentration were investigated since the H$_2$O$_2$ decomposition rate could represent the magnitude of the ZrO$_2$ abrasive dispersant stability in the slurry, as shown in Figure 1. EA, PA, MPP, and MAP correspond to etidronic acid with double-negatively charged phosphate ions, phosphorous acid with a single negatively charged phosphite ion, monopotassium phosphate with a single negatively charged phosphite ion, and monoammonium phosphate with a single negatively charged phosphate ion, respectively, as shown by the chemical symbols in Figure 1. The H$_2$O$_2$ decomposition rate (i.e., H$_2$O$_2$ concentration/h) was estimated by measuring the slope of the remaining H$_2$O$_2$ concentration to the progress time after H$_2$O$_2$ was added to the slurry (i.e., the progress time), as shown in Figure S1. Note that the H$_2$O$_2$ concentration for all CMP slurries, including a scavenger, decreased when the progress time increased, and the slope of the remaining H$_2$O$_2$ concentration to the progress time indicates the H$_2$O$_2$ decomposition rate. In addition, a lower H$_2$O$_2$ decomposition rate implies a higher improvement in the stability of the ZrO$_2$ abrasive dispersant in the W-film surface CMP slurry. For all four different phosphite or phosphate-based-scavengers, the H$_2$O$_2$ decomposition rate decreased rapidly from 0.0037 wt%/h to less than 0.0020 wt%/h as soon as a scavenger of 0.05 wt% was added to the W-film surface CMP slurry, and the H$_2$O$_2$ decomposition rate decreased linearly with increasing scavenger concentration, as shown in Figure 1. In addition, a lower sequence of the H$_2$O$_2$ decomposition rate at 0.25 wt% scavenger concentration was presented by EA (i.e., 0.0008 wt%/h), PA (i.e., 0.0012 wt%/h), MPP
(i.e., 0.0016 wt%/h), and MAP (i.e., 0.0017 wt%/h), indicating that the higher sequence of the improvement effect of the ZrO₂ abrasive dispersant stability in the slurry was followed by EA, PA, MPP, and MAP. In particular, the higher sequence of the decrease in the slope of the H₂O₂ decomposition rate to the scavenger concentration (i.e., Fenton-reaction ability) was followed by EA (i.e., 0.0097 H₂O₂ wt%/h/EA wt%), PA (i.e., 0.0083 H₂O₂ wt%/h/EA wt%), MPP (i.e., 0.0067 H₂O₂ wt%/h/EA wt%), and MAP (i.e., 0.0063 H₂O₂ wt%/h/EA wt%), as shown in Figure 1. The dependency of the H₂O₂ decomposition rate on the molecular structure of the scavengers was related to the mole concentration and the dissociation constant of protonated phosphite or phosphate ions, as shown in Figure S2. There were two groups of scavengers, i.e., those with protonated phosphite ions (i.e., EA and PA) and those with phosphate ions (i.e., MPP and MAP). At the same scavenger mole concentration, the effect of the scavengers with protonated phosphite ions (i.e., H₂O₂ decomposition rate) was better than that of those with protonated phosphate ions. Among scavengers with protonated phosphite ions, at the same scavenger mole concentration, EA showed a higher scavenger effect than PA, since EA contained two protonated phosphite ions while PA had one protonated phosphite ion. Otherwise, among the scavengers with protonated phosphate ions, MPP showed a slightly higher scavenger effect than MAP, since the dissociation of the protonated phosphate ion in MAP (i.e., NH₄⁺) was much more difficult than that in MPP (i.e., K⁺). Note that the dissociation constant of NH₄⁺ in MAP was Kₐ = 1.8 × 10⁻⁵. This result also indicates that a higher sequence of the ZrO₂ abrasive dispersant stability improvement effect was achieved by EA, PA, MPP, and MAP. In summary, the addition of a phosphite or a phosphate-based scavenger to the W-film surface CMP slurry significantly reduced the H₂O₂ decomposition rate, which clearly improved the ZrO₂ abrasive dispersant stability in the slurry. In addition, the H₂O₂ decomposition ratio decreased linearly with the scavenger concentration, so that the improvement in the magnitude of the ZrO₂ abrasive dispersant stability in the slurry would be enhanced by increasing the scavenger concentration. Moreover, the magnitude of improvement of the ZrO₂ abrasive dispersant stability in the slurry strongly depended on the scavenger type; that is, a higher sequence of the improvement magnitude of the ZrO₂ abrasive dispersant stability in the slurry was followed by EA, PA, MPP, and MAP.

Figure 1. Dependency of the H₂O₂ decomposition rate on the scavenger type and concentration.

3.2. Dependency of W- and SiO₂-Film Polishing Rate on Scavenger Type and Concentration

To estimate the influence of the chemical properties of the scavenger on the chemical-mechanical-polishing performance of W- and SiO₂-film surfaces, the W- and SiO₂-film surface polishing rates were investigated as a function of the scavenger type (i.e., EA, PA, MPP, and MAP) and concentration in the CMP slurries, as shown Figure 2. For all W-film surface CMP slurries including a scavenger, the W-film surface polishing rate decreased
linearly and rapidly from ~110.1 to ~17.8 nm/min when the scavenger concentration increased from 0 to 0.25 wt%. To distinguish the detailed W-film surface polishing rate among scavengers, the magnified W-film surface polishing rate vs. scavenger concentration in Figure 2a was magnified, as shown in Figure 2b. The lower sequence of the W-film surface polishing rate at the same scavenger concentration was clearly presented by EA, PA, MPP, and MAP, although their difference was less. The dependency of the H$_2$O$_2$ decomposition rate on the scavenger type in Figure 1 was well correlated with that of the W-film surface polishing rate (Figure 2b); that is, a lower H$_2$O$_2$ decomposition rate led to a lower W-film surface polishing rate. A lower H$_2$O$_2$ decomposition rate produced a lower magnitude of chemical oxidation (i.e., WO$_3$) on the W film surface via the Fenton reaction during CMP, as shown in Equations (1)–(12). Thus, since the lower sequence of the H$_2$O$_2$ decomposition rate was followed by EA, PA, MPP, and MAP, the lower sequence of the W-film surface polishing rate was presented by EA, PA, MPP, and MAP, as shown in Figure 2b.

Figure 2. CMP performance of W-film surface slurries. (a) W- and SiO$_2$-film surface polishing rates depending on the scavenger type and concentration; (b) magnified W- and SiO$_2$-film surface polishing rates from (a).

Otherwise, for all W-film surface CMP slurries including a scavenger, the SiO$_2$-film surface polishing rate increased significantly with the scavenger concentration up to a specific scavenger concentration and then decreased remarkably with increasing scavenger concentration. This result indicates that the SiO$_2$-film polishing rate peaks at a specific scavenger concentration. The mechanism by which the SiO$_2$-film polishing rate peaks at a specific scavenger concentration will be discussed later. The scavenger concentrations showing a peaked SiO$_2$-film surface polishing rate for the CMP slurries including EA, PA, MPP, and MAP were 0.10, 0.15, 0.15, and 0.15 wt%, respectively. The higher sequence of the peaked SiO$_2$-film surface polishing rate for the CMP slurries including a scavenger was presented by EA (i.e., 44.3 nm/min), PA (i.e., 27.0 nm/min), MPP (i.e., 26.3 nm/min), and MAP (i.e., 24.9 nm/min), as shown in Figure 2b. The dependency of the peaked SiO$_2$-film surface polishing rate on the scavenger type as shown in Figure 1 is also well correlated with that of the H$_2$O$_2$ decomposition rate as shown in Figure 2b; that is, a lower H$_2$O$_2$ decomposition rate led to a higher SiO$_2$-film surface polishing rate. Since a lower H$_2$O$_2$ decomposition rate generates lower dissolved O$_2$ and radicals (i.e., OH$^\cdot$, HO$_2^\cdot$, and O$_2^{2-}$), it would perform as a higher SiO$_2$-film surface polishing rate because of chemical oxidation between the Si(OH)$_4$-film surface and radicals (i.e., OH$^\cdot$, HO$_2^\cdot$, and O$_2^{2-}$). Note that the SiO$_2$-film surface would be transformed from SiO$_2$ to Si(OH)$_4$ via a hydrolysis reaction in the CMP slurry. Thus, since a lower sequence of the H$_2$O$_2$ decomposition rate in the slurry was presented by EA, PA, MPP, and MAP, a higher sequence of SiO$_2$-film surface polishing rate was shown by EA, PA, MPP, and MAP.
3.3. Dependencies of Chemical Properties (i.e., Corrosion, Potentiodynamic Polarization, and Chemical Composition) on Scavenger (i.e., EA) Concentration

To understand the mechanism of the dependencies of the W- and SiO$_2$-film surface polishing rate on the scavenger concentration, etidronic acid with double-negatively charged phosphate ions (i.e., EA) was selected. Again, the dependence of the abrasive dispersant stability on the scavenger concentration (i.e., EA) was investigated by measuring the time-dependent secondary abrasive size in the W-film surface CMP slurries after mixing H$_2$O$_2$ with the CMP slurry, as shown in Figure 3a. For all CMP slurries with different scavenger concentrations, the secondary abrasive size rapidly increased with the progress time after mixing H$_2$O$_2$ with the CMP slurry at a specific time (called the H$_2$O$_2$ pot lifetime). However, the pot lifetime increased linearly from 47 to 1401 h when the scavenger concentration increased from 0 to 0.25 wt%, as shown in Figure 3b. This result was well correlated with the H$_2$O$_2$ decomposition rate (Figure 1); that is, the H$_2$O$_2$ pot lifetime increased exponentially when the H$_2$O$_2$ decomposition rate decreased. Surprisingly, the H$_2$O$_2$ pot lifetime enhanced from 47 to 335 h, although the EA of 0.05 wt% was added to the W-film surface CMP slurry, indicating that the addition of the scavenger (i.e., EA) is very effective for achieving a better ZrO$_2$ abrasive dispersant stability in the slurry.

![Figure 3](image_url)

*Figure 3. Effect of scavenger (i.e., EA) on the ZrO$_2$ abrasive stability in W-film surface slurries mixed with 1.5 wt% H$_2$O$_2$. (a) Secondary abrasive size vs. the progress time after mixing H$_2$O$_2$ into the W-film surface slurries, depending on the scavenger (i.e., EA) concentration. (b) H$_2$O$_2$ pot lifetime depending on the scavenger concentration. The inset represents the correlation between H$_2$O$_2$ pot lifetime and H$_2$O$_2$ decomposition rate.*

To understand how the addition of a scavenger to the W-film surface CMP slurry affects the morphology of the W-film surface, the dependencies of the magnitude of corrosion and surface morphology on the scavenger concentration were estimated by measuring the static etch rate at 65 °C for 3 min and by observing the SEM images after etching, as shown in Figure 4. The static etch rate (i.e., magnitude of corrosion) increased significantly from 1.3 to 5.6 nm/min when the scavenger (i.e., EA) concentration increased from 0 to 0.25 wt%. Note that the reason for the corrosion (i.e., etching) on the W-film surface via the addition of the scavenger (i.e., EA) could be understood by considering the chemical reaction between WO$_3$, (C$_2$H$_6$O$_7$P$_2$)$_2$-$^-$, and O$_2$, producing WO$_4^{2-}$, CO$_2$, H$_2$O, and H$_2$PO$_3$-$^-$ as shown in Equation (15). In addition, the surface morphology induced by corrosion increased significantly with the scavenger concentration, as shown in the background SEM images in Figure 4. This result indicates that the addition of a scavenger (i.e., EA) to the W-film surface CMP slurry could etch the W-film surface so that the W-film surface roughness was remarkably enhanced by etching at the grain boundaries of the poly-W-film surface. Thus, the size of the corrosion-induced pits increased notably with the scavenger concentration, as shown in the lateral line profiles of the surface roughness in Figure 4.
Figure 4. Corrosion magnitude (i.e., static etch rate) and corrosion-induced surface morphology depending on the scavenger (i.e., EA) concentration. (a) EA of 0.00 wt%; (b) EA of 0.05 wt%; (c) EA of 0.10 wt%; (d) EA of 0.15 wt%; (e) EA of 0.20 wt%; (f) EA of 0.25 wt%. Background SEM images show the presence and magnitude of corrosion on the W-film surface after dipping the W-film into the CMP slurry with a scavenger (i.e., EA). The lateral profiles of image contrast on the SEM images correspond to the magnitude of corrosion.

To characterize how the addition of the scavenger (i.e., EA) to the W-film surface CMP slurry influences the magnitude of corrosion, the potentiodynamic polarizations of the W-film surfaces were observed as a function of the scavenger concentration, as shown in Figure 5. The presence of a porous chemical oxide layer on the W-film surface was found at the anode curve of the potentiodynamic polarization curve, as shown in the circle of Figure 5. The formation magnitude of the porous chemical oxide layer increased with the scavenger concentration, as shown in the magnified figure of the anode curve (i.e., the upper inset of Figure 5). From the potentiodynamic polarization curve, the dependencies of the corrosion potential (E_{corr}) and corrosion current (I_{corr}) were calculated using the Tafel method, as shown in the inset of Figure 5 [18]. E_{corr} decreased linearly from 0.47 to 0.19 V while I_{corr} increased significantly and linearly from 10^{-5.8} to 10^{-3.9} A/cm², when the scavenger concentration increased from 0 to 0.25 wt%, meaning that the formation magnitude of porous WO₃ layer on the W-film surface was noticeably enhanced with the scavenger concentration. These results imply that the addition of a scavenger to the W-film surface CMP slurry could enhance the magnitude of corrosion (i.e., formation magnitude of the porous chemical oxide layer). In addition, the dependence of the static etch rate on the scavenger concentration was well correlated with that of the I_{corr} on the scavenger concentration; that is, both I_{corr} and the static etch rate increased linearly and significantly with the scavenger concentration. Thus, the W-film surface polishing rate decreased linearly and significantly with the scavenger concentration, since the W-film surface polishing rate generally decreased with both the static etch rate and the formation magnitude of the porous oxide layer on the W-film surface [10].
To confirm the dependence of the chemical oxidation magnitude of the W-film surface on the scavenger concentration, the chemical composition (i.e., relative intensity of W-metal and WO$_3$) of the W-film surface was analyzed as a function of the scavenger concentration using XPS. Reminders that the W-film surface could be chemically oxidized, as shown in Equations (13)–(14). In XPS, W metal 4f$7/2$ and 4f$5/2$ peaks were found at 31.6 and 33.8 eV, and those of WO$_3$ peaks are located at 35.6 and 37.8 eV [19,20], respectively, as shown in Figure 6a. The normalized XPS-peak intensity at WO$_3$ decreased almost linearly with increasing scavenger concentration, as shown in Figure 6b. Otherwise, the normalized XPS-peak intensity at the W-metal increased almost linearly with the scavenger concentration. These results indicate that the addition of a scavenger to the W-film surface CMP slurry evidently reduced the chemical oxidation magnitude (i.e., WO$_3$) on the W-film surface; that is, the chemical oxidation magnitude on the W-film surface decreased clearly with increasing scavenger concentration. The dependence of the normalized XPS-peak intensity of WO$_3$ on the W-film surface on the scavenger concentration was well calibrated with those of the static etch rate (i.e., corrosion) and corrosion current (i.e., $I_{corr}$) on the scavenger concentration; that is, a lower normalized XPS-peak intensity of WO$_3$ corresponded to a higher static etch rate and $I_{corr}$. Moreover, the dependence of the hydrolysis magnitude of the SiO$_2$-film surface on the scavenger concentration was observed as a function of the scavenger concentration using XPS, as shown in Figure 6c. The XPS-peak intensities of Si–O–Si, Si–OH, and SiO$_2$ on the SiO$_2$-film surface were presented at 101.5, 102.3, and 103.4 eV, respectively [21,22]. Note that the normalized intensity of Si–OH (i.e., hydrolysis magnitude) determines the SiO$_2$-film polishing rate [10]; that is, a higher normalized intensity of Si–OH leads to a higher SiO$_2$-film polishing rate, since chemical-dominant CMP was conducted by rubbing ZrO$_2$ abrasives and a nanoscale thick Si–OH layer on the SiO$_2$-film surface. After CMP, the normalized XPS-peak intensity of Si–OH on the SiO$_2$-film surface peaked at a scavenger concentration of 0.10 wt%, while that of SiO$_2$ on the SiO$_2$-film surface was minimized at the same scavenger concentration. These results indicate that the normalized XPS-peak intensity of Si–OH on the SiO$_2$-film surface depending on the scavenger concentration was well correlated with the SiO$_2$-film polishing rate depending on the scavenger concentration. A higher normalized XPS-peak intensity of Si–OH on the SiO$_2$-film surface led to a higher SiO$_2$-film polishing rate. However, since the chemical
properties (i.e., the amount of dissolved O$_2$ and radicals) decreased linearly with increasing scavenger concentration, the normalized XPS-peak intensity of Si–OH on the SiO$_2$-film surface depending on the scavenger concentration could not be directly understood by considering only a chemical-dominant CMP mechanism.

![Figure 6](image_url)

**Figure 6.** Chemical composition of W- and SiO$_2$-film surfaces depending on the scavenger (i.e., EA) concentration and analyzed by XPS after the W-film surface CMP, depending on the scavenger (i.e., EA) concentration, (a) Spectra XPS intensity vs. binding energy of WO$_3$ and W-metal on the W-film surface; (b) normalized XPS peak percentage of WO$_3$ and W-metal on the W-film surface; (c) spectra intensity vs. binding energy of Si–O–Si, SiO$_2$, and Si–OH on the SiO$_2$-film surface, and (d) normalized XPS peak percentage of Si–O–Si, SiO$_2$, and Si–OH on the SiO$_2$-film surface after CMP.

3.4. Dependency Mechanism of W- and SiO$_2$-Film Surface Polishing Rates on Scavenger Concentration

In general, both W- and SiO$_2$-film surface polishing rates are principally determined by both chemical- and mechanical-dominant CMP. The hardness of the W-film surface (i.e., 6.64 GPa) is significantly lower than the SiO$_2$-film surface (i.e., 11.62 GPa), as shown in Figure S3, revealing that the W-film surface polishing rate is determined by chemical-dominant CMP (i.e., corrosion and magnitude of chemical oxidation) rather than a mechanical-dominant CMP (i.e., electrostatic force between the abrasives and the W-film surface). Since the normalized XPS-peak intensity of the chemical oxidation magnitude (i.e., WO$_3$) decreased significantly with increasing scavenger (i.e., EA) concentration and both the
static etch rate (i.e., magnitude of corrosion) and corrosion current increased significantly with the scavenger concentration, the W-film surface polishing rate decreased remarkably with increasing scavenger concentration. To confirm that the W-film surface polishing rate is determined by a chemical-dominant CMP rather than a mechanical-dominant CMP, the dependence of the electrostatic force between the ZrO₂ abrasive and WO₃ layer on the W-film surface was estimated as a function of the scavenger (i.e., EA) concentration, as shown in Figure 7a. Note that the zeta potential of the WO₃ layer and W-film surface was measured by the zeta potential of WO₃ particles in the W-film surface CMP slurry, since the zeta potential of the W-film surface could not be directly measured by a particle analyzer because of the metallic characteristic of the W-film surface. Thus, the zeta potential of the WO₃ particles responds to that of the WO₃ layer on the W-film surface. The zeta potential of ZrO₂ abrasives decreased from +5.5 to +1.4 mV when the scavenger concentration increased from 0 to 0.10 wt% and then it changed from a positive to a negative zeta potential and negatively increased significantly from +1.4 to −13.5 mV for further increase in scavenger-concentration. The zeta potential of the W-film surface decreased from +20.3 to +1.4 mV when the scavenger concentration increased from 0 to 0.10 wt%. Then, it transited from a positive to a negative zeta potential and negatively increased considerably from +1.4 to −10.4 mV for further increase in scavenger-concentration. As a result, the repulsive electrostatic force between the ZrO₂ abrasive and the W-film surface decreased significantly from 112.5 to 2.0 abs. up to the EA of 0.10 wt% and then it increased remarkably for further increase in scavenger concentration, as shown in Figure 7b. Thus, if the W-film surface polishing rate is principally determined by a mechanical-dominant CMP, it would increase with the scavenger concentration increasing up to the EA of 0.10 wt% and then decreased with the scavenger concentration for further increase in EA-concentration; that is, the W-film polishing rate should be peaked at the EA of 0.10 wt%. Note that a higher repulsive electrostatic force results in a lower mechanical polishing rate. Therefore, since the W-film surface polishing rate decreased significantly with increasing scavenger (i.e., EA) concentration, the W-film surface CMP mechanism would be principally performed by chemical-dominant CMP rather than mechanical-dominant CMP.

Figure 7. Dependencies of mechanical-dominant CMP properties on the scavenger concentration (i.e., EA). (a) Zeta potentials of ZrO₂ abrasives, WO₃ particles, and SiO₂ particles depending on the scavenger (i.e., EA) concentration, and (b) electrostatic forces between ZrO₂ abrasives and WO₃ particles as well as between ZrO₂ abrasives and SiO₂ particles.
In order to test whether the mechanism of the SiO\(_2\)-film surface CMP is a chemical-dominant CMP or a mechanical-dominant CMP, the influence of the Fenton reaction in the CMP slurry including a scavenger was reviewed by considering Equations (16)–(19).

\[
\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4
\]  
(16)

\[
\text{Si(OH)}_4 + 4\text{OH}^* \rightarrow \text{SiO}_2 + \text{H}_2\text{O} + \text{O}_2
\]  
(17)

\[
2\text{Si(OH)}_4 + 2\text{O}_2^{*-} \rightarrow 2\text{SiO}_2 + 4\text{H}_2\text{O} + 2\text{O}_2
\]  
(18)

\[
3\text{Si(OH)}_4 + 4\text{HO}_2^* \rightarrow 3\text{SiO}_2 + 8\text{H}_2\text{O} + 3\text{O}_2
\]  
(19)

Since a lower \(\text{H}_2\text{O}_2\) decomposition rate produced a lower amount of dissolved \(\text{O}_2\) and radicals (i.e., \(\text{OH}^*, \text{HO}_2^*\) and \(\text{O}_2^{*-}\)) via the Fenton reaction, the SiO\(_2\)-film surface would be chemically oxidized rather than chemically etched, as shown in Equations (16)–(19). Note that the SiO\(_2\)-film surface transformed the Si(OH)\(_4\)-film surface via a hydrolysis reaction, as shown in Equation (16), and then the Si(OH)\(_4\)-film surface is oxidized via a chemical reaction with radicals (i.e., \(\text{OH}^*, \text{HO}_2^*\) and \(\text{O}_2^{*-}\)) by producing \(\text{H}_2\text{O}_2\) and \(\text{O}_2\), as shown in Equations (17)–(19). Note that a higher chemical oxidation magnitude leads to a less SiO\(_2\)-film surface polishing rate. Thus, a lower \(\text{H}_2\text{O}_2\) decomposition rate corresponding to a higher scavenger (i.e., EA) concentration leads to a higher SiO\(_2\)-film surface polishing rate. However, the SiO\(_2\)-film surface polishing rate peaked at a specific scavenger concentration (i.e., EA of 0.10 wt%), as shown in Figure 2, indicating that the mechanism of the SiO\(_2\)-film surface CMP could not be analyzed with only a chemical-dominant CMP. Thus, a mechnical-dominant CMP characteristic (i.e., the electrostatic force between ZrO\(_2\) abrasives and SiO\(_2\)-film surface) in the CMP slurry was investigated as a function of the scavenger concentration, as shown in Figure 7b. Note that the zeta potential of the SiO\(_2\)-film surface in the CMP slurry is represented by the zeta potential of the SiO\(_2\) particles in the CMP slurry. The attractive electrostatic force between ZrO\(_2\) abrasives and the SiO\(_2\)-film surface in the CMP slurry decreased noticeably from 36.1 to 18.5 abs., when the scavenger concentration increased from 0 to 0.10 wt%. Thus, the SiO\(_2\)-film surface polishing rate decreased with the scavenger concentration, since a higher attractive force between ZrO\(_2\) abrasives and the SiO\(_2\)-film surface generally leads to a higher SiO\(_2\)-film surface polishing rate [10], which was the opposite of the SiO\(_2\)-film surface trend. This result indicates that up to a scavenger (i.e., EA) concentration of 0.10 wt%, the mechanism of the SiO\(_2\)-film surface CMP follows a chemical-dominant CMP, since the dissolved \(\text{O}_2\) and radicals (i.e., \(\text{OH}^*, \text{HO}_2^*\), and \(\text{O}_2^{*-}\)) decreased with increasing scavenger concentration. However, the repulsive electrostatic force between the ZrO\(_2\) abrasives and the SiO\(_2\)-film surface in the CMP slurry increased rapidly from 18.5 to 229.9 abs., when the scavenger concentration increased from 0.10 to 0.25 wt%. Thus, the SiO\(_2\)-film surface polishing rate decreased with increasing scavenger concentration, since a higher repulsive force between the ZrO\(_2\) abrasives and the SiO\(_2\)-film surface generally leads to a lower SiO\(_2\)-film surface polishing rate [10]. This result means that, for a scavenger (i.e., EA) concentration above 0.10 wt%, the mechanism of the SiO\(_2\)-film surface CMP is principally associated with a mechanical-dominant CMP rather than a chemical-dominant CMP, although the dissolved \(\text{O}_2\) and radicals (i.e., \(\text{OH}^*, \text{HO}_2^*\), and \(\text{O}_2^{*-}\)) decreased with increasing the scavenger concentration. Therefore, the mechanism of the SiO\(_2\)-film surface polishing rate for a scavenger (i.e., EA) concentration ranging between 0 and 0.10 wt% was followed by a chemical-dominant CMP. On the other hand, the mechanism of the SiO\(_2\)-film surface polishing rate for a scavenger (i.e., EA) concentration ranging between 0.10 and 0.25 wt% was conducted by a mechanical-dominant CMP. Thus, the SiO\(_2\)-film surface polishing rate peaked at a specific scavenger concentration (i.e., 0.10 wt%).

For a practical application as a W-film surface CMP slurry, since the addition of a scavenger to a W-film surface CMP slurry could induce a corrosion of the W-film surface during CMP, although it significantly improves the abrasive dispersant stability in the slurry, a corrosion inhibitor with a protonated amine-functional group (i.e., \(\text{C}_4\text{H}_8\text{N}_2\text{O}_3\)):
asparagine) of 0.1 wt% was additionally mixed with the W-film surface slurry including the scavenger (i.e., EA). The static etch rate was 0.75–0.85 nm/min, which was independent of the scavenger concentration, as shown in Figure S4. Thus, the addition of a corrosion inhibitor could prevent the generation of corrosion on the W-film surface. In addition, it was found that there was almost no difference in the W-film surface polishing rate depending on the scavenger concentration between the CMP slurry with and without a corrosion inhibitor, as shown in Figure S5. Therefore, the addition of a corrosion inhibitor to the W-film surface CMP slurry with a scavenger (i.e., EA) could achieve W-film surface CMP without the presence of corrosion on the W-film surface after CMP, as shown in Figure S6.

4. Conclusions

For advanced semiconductor devices such as AP, DRAM, and 3D NAND flash memory, the frequency of the W-film surface CMP has rapidly increased. In W-film surface CMP, the Fenton reaction should be utilized to enhance the W-film surface polishing rate by forming a nanoscale thick chemically oxidized WO$_3$ layer on the W-film surface. However, the produced radicals (i.e., OH$^\bullet$, HO$_2^\bullet$ and O$_2^{\bullet-}$) via the Fenton reaction between the ferric–ionic catalyst and H$_2$O$_2$ directly degrades the magnitude of the abrasive dispersant stability in the W-film surface CMP slurry. As a solution, the addition of a scavenger to the W-film surface CMP slurry is essential, as it can significantly suppress the H$_2$O$_2$ decomposition rate and the amount of radicals can be noticeably reduced. Unlike a scavenger with a carboxyl functional group [10], a scavenger with phosphite (i.e., EA and PA) or phosphate (i.e., MPP and MAP) presented an incredible improvement in the abrasive dispersant stability in the W-film surface CMP. In particular, the improvement in the magnitude of the abrasive dispersant stability was remarkably enhanced with the scavenger concentration. Moreover, it was found that a higher improvement magnitude of the abrasive dispersant stability in the W-film surface CMP slurry was followed by EA, PA, MPP, and MAP, since a lower sequence of a H$_2$O$_2$ decomposition rate was performed by EA, PA, MPP, and MAP. However, the addition of a scavenger with double-negatively charged phosphite ions could induce corrosion on the W-film surface via a chemical reaction between WO$_3$ and the ionized EA (i.e., (C$_2$H$_6$O$_7$P$_2$)$_2^{2-}$) so that the W-film surface polishing rate decreased linearly and significantly with increasing scavenger concentration. In addition, the amount of dissolved O$_2$ to form WO$_3$ on the W-film surface via the Fenton reaction to decompose H$_2$O$_2$ significantly decreased with increasing scavenger (i.e., EA) concentration. Thus, due to the presence of corrosion and the reduction of the dissolved O$_2$ amount by adding a scavenger to the W-film surface CMP slurry, the W-film surface polishing rate decreased notably with increasing scavenger concentration. These results indicate that the mechanism of the W-film surface CMP depending on the scavenger concentration in the W-film surface CMP slurry was principally determined by chemical-dominant CMP.

The addition of a scavenger to the W-film surface CMP slurry could influence the SiO$_2$–film surface polishing rate depending on the scavenger concentration as well as the mechanism of the SiO$_2$–film surface CMP. Since the amount of dissolved O$_2$ and radicals (i.e., OH$^\bullet$, HO$_2^\bullet$ and O$_2^{\bullet-}$) in the W-film surface CMP slurry via the Fenton reaction decreased significantly with increasing scavenger concentration, chemical oxidation via chemical reaction between the hydrolyzed Si(OH)$_4$ surface, dissolved O$_2$, and radicals was notably enhanced with increasing scavenger concentration. As a result, at the scavenger concentration between 0 and 0.10 wt%, the SiO$_2$–film surface polishing rate increased noticeably with the scavenger concentration, which was mainly determined by chemical-dominant CMP. Otherwise, above the scavenger concentration of 0.10 wt%, since the repulsive electrostatic force between the negatively charged ZrO$_2$ abrasive and SiO$_2$–film surface increased rapidly with the scavenger concentration, the SiO$_2$–film surface decreased significantly with increasing scavenger concentration. As a result, the SiO$_2$–film surface polishing rate peaked at a specific scavenger concentration, indicating that the mechanism of the SiO$_2$–film surface CMP was chemical dominant as well as mechanical-dominant.
CMP. The negative effect of the presence of corrosion on the W-film surface could be eliminated by adding a corrosion inhibitor with a carboxyl functional group without an additional decrease in the W- and SiO$_2$-film surface polishing rate. Therefore, the addition of a scavenger with phosphite (i.e., EA and PA) or phosphate (i.e., MPP and MAP) to the W-film surface CMP slurry could remarkably improve the abrasive dispersant stability in the W-film surface CMP slurry for practical CMP applications in semiconductor devices. Further studies would be necessary for another ferric–ionic catalyst for the Fenton reaction such as ammonium iron(III) citrate, ammonium iron(III) oxalate trihydrate, iron(III) chloride hexahydrate, iron(III) sulfate hydrate, and Potassium ferrocyanide. In addition, the improvement effect of the abrasive dispersant stability using these catalysts, including a scavenger with phosphate or phosphate ions, is necessary for further research. Therefore, the chemical design of a scavenger in the slurry for the W-film surface CMP via the Fenton reaction would be key to achieving a higher W- and a proper SiO$_2$-film polishing rate as well as a longer abrasive dispersant stability.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/nano11123296/s1: Figure S1: Dependencies of the ZrO$_2$ abrasive stability in the W-film-surface slurry mixed with the oxidant (i.e., H$_2$O$_2$) as a function of the scavenger type and concentration. The H$_2$O$_2$ decomposition-rate as a function of the progress time after mixing H$_2$O$_2$ into the W-film-surface slurries with (a) EA, (b) PA, (c) MPP and (d) MAP; Figure S2: H$_2$O$_2$ decomposition rate depending on scavenger type and mole concentration; Figure S3: Hardness of W-, TiN-, SiO$_2$-, and poly-Si-film.; Figure S4: Effect of corrosion inhibitor on suppressing the degree of corrosion (i.e., static etch rate) and surface morphology. Background SEM images show the presence and degree of corrosion on the W-film-surface after dipping the W-film into the CMP slurry including a scavenger (i.e., EA). The lateral profile of image contrast on the SEM images corresponded to the degree of corrosion. The addition of the corrosion inhibitor (i.e., asparagine) in the W-film-surface slurry with a scavenger (i.e., EA) suppressed remarkably the corrosion degree (i.e., static etch rate); Figure S5: Effect of a corrosion inhibitor (i.e., asparagine) on CMP performance of W-film-surface slurries, including a scavenger (i.e., EA). (a) Dependencies of W-and SiO$_2$-film-surface polishing rate on the scavenger concentration for the W-film-surface slurry including both scavenger (i.e., EA) and corrosion inhibitor (i.e., asparagine) and (b) magnified W- and SiO$_2$-film-surface polishing rates depending on the scavenger concentration from (a). The addition of the corrosion inhibitor (i.e., asparagine) in the W-film-surface slurry with a scavenger (i.e., EA) showed no change of W- and SiO$_2$-film-surface polishing rates; Figure S6: Potentiodynamic polarization curves of the W-film surface depending on the scavenger (i.e., EA) concentration and corrosion inhibitor (i.e., asparagine). The upper inset showed none of the surface chemical oxidation. The lower inset represented both corrosion potential (i.e., $E_{corr}$) and corrosion current (i.e., $I_{corr}$), which was independent of the scavenger concentration.

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