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Characterization of 5-Aminotetrazole as a Corrosion Inhibitor in Copper Chemical Mechanical Polishing

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In the Cu metallization process, it is important to prevent corrosion and recession of metal lines resulting from chemical reactions during the chemical mechanical polishing (CMP) process. In this paper, 5-aminotetrazole (ATRA) is investigated as a corrosion inhibitor for Cu CMP. In the wet etch test, it was found that the etch rate of ATRA decreased with concentration. The potentiodynamic polarization test and chronoamperometry test results revealed that ATRA could inhibit the Cu surface against corrosion more effectively than benzotriazole (BTA) below 0.01 M. Fourier transform infrared and ultraviolet-visible analysis clearly demonstrated that ATRA dissociated more easily in all pH ranges and could be polymerized faster and more effectively than BTA. Therefore, both corrosion and recession could be considerably reduced after CMP by using slurry containing ATRA. Furthermore, from the results of defect review after CMP, it was found that defects such as slurry residue, pit corrosion, and particles were effectively prevented due to small molecular size and high solubility of ATRA.
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Recently, in metallization processes, Cu has replaced other materials such as W and Al due to its low electrical resistance and high resistance to electromigration.[1-3] In patterning Cu, $CuCl_2$, which is a nonvolatile by-product of the dry etchback process, inhibits further Cu etching. Therefore, Cu metallization has been altered from the dry etchback process into the damascene technique, in which chemical mechanical polishing (CMP) is used to remove the protruding material and planarize the wafer surface.

To achieve successful Cu metallization, it is important to minimize metal loss during the CMP process, because the remaining metal line height is directly related to the operation speed of the device. In general, it is known that Cu dishing, corrosion, and oxide erosion become the main reasons for metal line loss, and these factors depend on pattern density and geometry.[4] They are strongly affected by the chemistry of the slurry.[5] Luo and Babu investigated the effect of concentration of the oxidizing agent and corrosion inhibitor, benzotriazole (BTA), on Cu dishing.

The corrosion inhibitor, which protects the recessed Cu layer from the chemical reaction, is a critical Cu slurry additive. At present, BTA is widely used to inhibit Cu corrosion and its properties and performance have been thoroughly investigated.[6-17] BTA reacts with Cu ions and produces an insoluble complex material, $[Cu^+BTA^-]_n$, which adsorbs on the surface, resulting in the inhibition of Cu corrosion by oxidizer.[18-27] Other organic inhibitors which are tetrazole compounds with similar structure and functional group have been minimally studied. Among the tetrazole compounds, 5-aminotetrazole (ATRA) as an inhibiting agent is investigated in this study. ATRA has an amine (NH_3^-) functional group, which is substituted with a hydrogen and three unpaired electrons. Because the ATRA has a cyclic molecular structure and more unpaired electrons, it can react with Cu ion more easily than BTA.

In this study, the inhibition effects of BTA and ATRA in the presence of H_2O_2 as an oxidizing agent and citric acid as a chelating agent in solution were investigated. The investigation was carried out using static etch rate and mechanical removal rate measurements, electrochemical studies, and surface chemistry analysis. Mechanical removal rate was obtained using a conventional polisher. The electrochemical studies were performed using a potentiostat/galvanostat tool. Fourier transform infrared (FTIR) and ultraviolet-visible (UV-vis) spectroscopy were used for the surface chemistry analysis.

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Experimental

Electrochemical measurements.— For the electrochemical experiments, a 99.9% Cu rod with a surface area of 0.5 cm^2 was used. A Pt electrode and a saturated calomel electrode (SCE) were assigned as a counter and a reference electrode, respectively. Potentiodynamic studies were performed with a EG&G model 263 potentiostat/galvanostat corrosion measurement system. The potentiodynamic polarization measurements were obtained with a scan rate of 20 mV/s and the potential ranged from −2 to 2 V.

A chronoamperometry test was applied to determine the inhibition efficiency of corrosion inhibitors. The experimental sequences were as follows.

A 1.5 × 1.5 cm Cu wafer connected with a wire was placed into the solution and then potential (0.3 V) was applied for 40 s to oxidize the Cu surface. An additional solution containing BTA or ATRA was added and the corrosion current density variation was measured.

Static dissolution study and analyses.— 1.5 × 1.5 cm Cu wafers with a structure of Cu [15,000 Å, electroplating (EP)] / Ta [250 Å, physical vapor deposition (PVD)] / TaN (100 Å, PVD) / poly Si were used to evaluate Cu etch rate in this study. Cu etch rate was calculated by measuring sheet resistance before and after the etch test. Wafers were dipped into solution for 30 min and then rapidly rinsed with deionized water and then measured.

To analyze an adsorption efficiency of corrosion inhibitor with Cu^0 or Cu^{2+}, FTIR and UV-vis spectrometry analyses were carried out, respectively.

Polishing test.— Single damascene patterned wafers with various line and space widths were prepared for the evaluation of dishing, pit corrosion, and defects in wide metal lines after CMP. Polishing tests were conducted using a polisher named Momentum, manufactured by Novellus Co. with 2.5 psi of down pressure, 600 rpm of table speed, 23 rpm of head speed, and 12 rpm/180° of arm speed. Polished wafers were cleaned with PC300C solution for 30 s. Line dishing and recess were evaluated using a P22 profilometer from KLA-Tencor Co., Ltd., and a field emission scanning electron microscopy (FESEM) tool. Corrosion and defectivity were measured using a KLA-6420 from KLA-Tencor Co., Ltd.

Preparing slurry.— To mix slurry for the polishing test, a colloidal-type alumina (α-Al_2O_3) based dispersion with 50-nm grain size and 30 wt % solids was used. The slurry was manufactured with several additives, including 2 wt % hydrogen peroxide, 0.02 M citric acid and pH controller, 0.1 M H_2SO_4, and 10 wt % KOH solution. The pH of the slurry was adjusted to 3 with pH controller.

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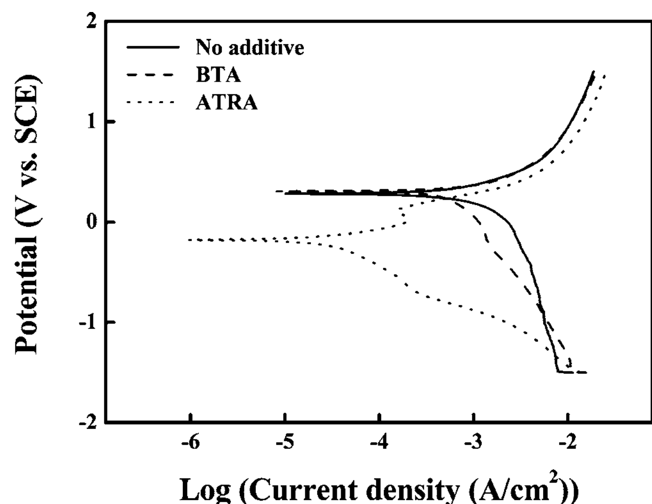

Figure 1. Potentiodynamic polarization curve of the pure Cu rod with a scan rate of 20 mV/s in solution basically containing 2 wt % of hydrogen peroxide and 0.02 M of citric acid: (a) no additive, (b) 0.01 M BTA, and (c) 0.01 M ATRA.

Results and Discussion

Electrochemical analysis results.— Figure 1 shows the potentiodynamic polarization curves of etched Cu in solution containing BTA or ATRA. BTA showed negligible change in the potentiodynamic polarization curve of Cu. However, in the case of ATRA, the corrosion current density markedly decreased from −3.15 to −4.76A/cm^2. A possible explanation is that complex compounds of ATRA and Cu ions are effectively inhibiting the oxidation reaction between Cu and hydrogen peroxide by being adsorbed on the Cu surface. Therefore, it is expected that Cu etch rate would decrease more when ATRA was added to the slurry.

Figure 2 represents the result of the linear polarization curves for Cu in solution of BTA or ATRA. From the results, it was measured that the slope of no additive, BTA, and ATRA is 75.19, 86.3, and 1609.3, respectively. Because the slope represents the corrosion resistance, the increase in the slope shows that corrosion becomes more inhibited.

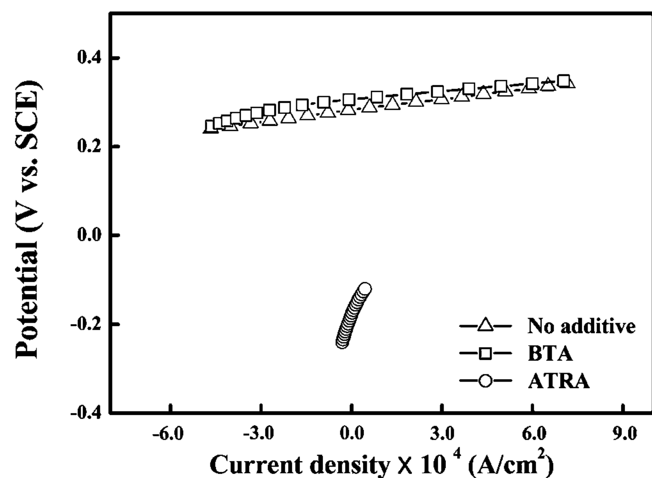

Figure 2. Linear polarization resistance of copper under static condition according to each corrosion inhibitor: (a) no additive, (b) 0.01 M BTA, and (c) 0.01 M ATRA.

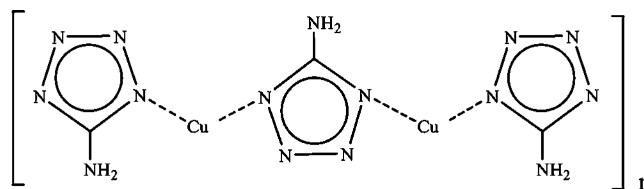

Figure 3. Suggested scheme of polymeric polymerization between 5-aminotetrazole and Cu^{2+}.

From the above results of Fig. 1 and 2, it can be concluded that ATRA passivates the Cu surface more effectively than BTA at the given concentration.

Generally, the Cu corrosion or dissolution progresses by consecutive reactions, as expressed in Eq. 1 and 2. The mechanism of Cu corrosion inhibition can be summarized like this. An activated layer is formed on the Cu surface after Cu loses an electron and becomes a cation (Eq. 1), and then the inhibitor, an anion, and unpaired electrons bond with the activated layer. Finally, a polymerized layer is formed on the Cu surface (Eq. 3), as suggested in Fig. 3, and thereafter the polymerized layer suppresses the oxidation reaction

$$\mathrm{Cu} \rightarrow \mathrm{Cu}^{+} + \mathrm{e} \qquad [1]$$

$$\mathrm{Cu}^{+} + \mathrm{CHELATOR} \rightarrow \mathrm{Cu\text{-}CHELATOR} \qquad [2]$$

$$\mathrm{Cu}^{2+} + \mathrm{INHIBITOR}^{-} \rightarrow [\mathrm{Cu\text{-}INHIBITOR}]_n \qquad [3]$$

Figure 4 shows the changes to anodic current flowing on the Cu surface and varying with the corrosion inhibitor concentration. Experiments were performed using a solution containing all of the additives except an abrasive. Before the inhibitor was added to the solution, about −600 to −700 μA/cm^2 of anodic current flowed on the Cu surface. The anodic current decreased immediately after the corrosion inhibitor was added to the solution. It was found that as the amount of inhibitor increased, anodic current decreased more and more. These results indicate that as more corrosion inhibitor was added to the solution, more layers were formed on the Cu surface.

The changes to the anodic current on the Cu surface vs the addition of BTA and ATRA are summarized in Table I. From Table I, it is clear that there were no significant differences in current densities between the two inhibitors when the concentration of inhibitor was over 0.01 M. Current density decreased more with ATRA than with BTA for concentrations less than 0.01 M, which demonstrates that ATRA performs better than BTA at lower concentration, probably due to differences in molecular structure and dissociation tendency. Because BTA has fewer unpaired electrons than ATRA and an inactive functional group, a benzene ring, it seems that BTA interaction with Cu ions is more likely to be interrupted than that of ATRA.

The FTIR analysis of BTA, ATRA, and their Cu complexes were carried out between 500 and 4000 cm^{-1}. The IR spectra of BTA as a function of pH are shown in Fig. 5a. In the case of pH 2, the presence of BTA over the oxide surface was well evidenced by the aromatic C–H stretch lying just above 3000 cm^{-1}. However, the adsorption peaks of BTA above pH 6 were not observed entirely, because the dissociation of hydrogen did not occur well and therefore, BTA could not make a reaction with Cu beyond pH 6. Meanwhile, in the case of ATRA shown in Fig. 5b, the evidence of adsorption of ATRA-Cu complexes on Cu surface, Cu–O vibration peak, was found at 1120 cm^{-1} and the presence of NH_2 stretch peak was at 2360 cm^{-1} in pH 2 and 6. The C–H stretch peak, which could be the evidence of existence of ATRA on copper oxide surface, was observed at over 3000 cm^{-1} in all pH conditions.

From the FTIR analysis results, it can be inferred that the adsorption ability was related with the dissociation tendency of each corrosion inhibitor. A comparison result of dissociation tendency be-

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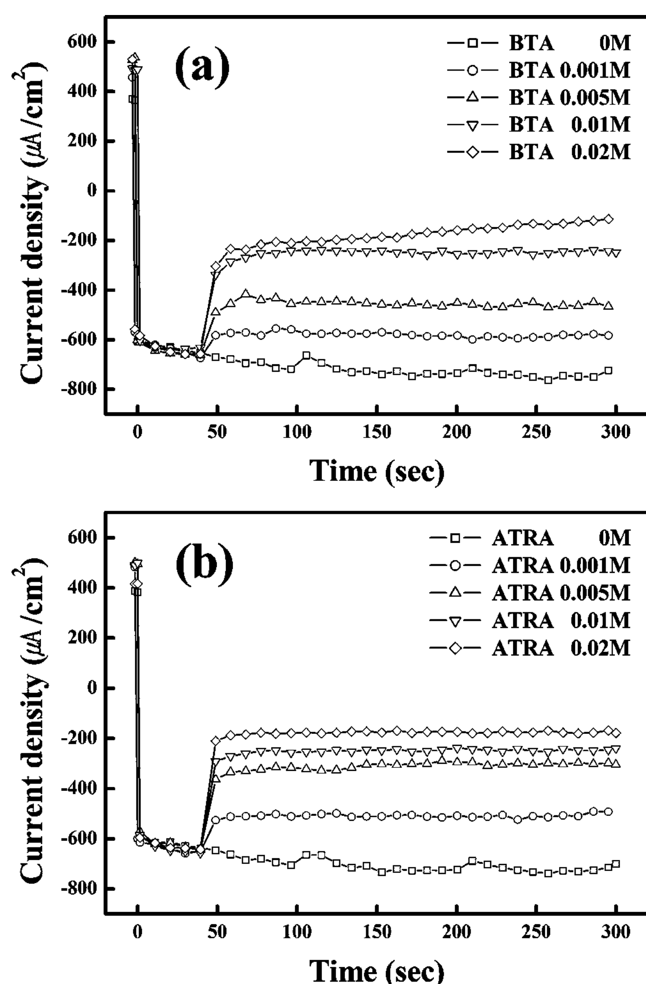

Figure 4. Behaviors of anodic current density according to the concentration of BTA and ATRA, which was added in deionized water: (a) BTA and (b) ATRA.

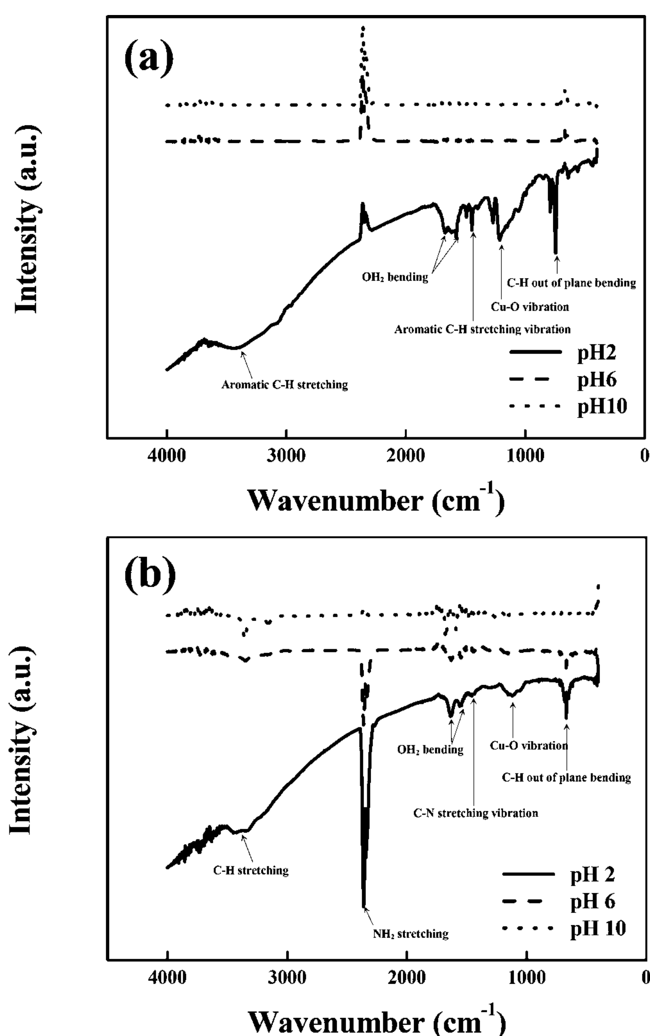

Figure 5. FTIR analysis results on Cu surface according to the solution pH after treatment of corrosion inhibitor: (a) BTA and (b) ATRA.

tween BTA and ATRA as a function of pH is summarized in Table II, where there were negligible changes after addition of corrosion inhibitors at pH 2, but the pH changes with ATRA were remarkable at pH 6 and 10 compared to BTA. Consequently, the dissociation tendency of ATRA is revealed to be higher than that of BTA over pH 6. This result suggests that the polymerization reaction of ATRA with a copper ion can be performed more effectively than that of BTA at the same concentration.

The passivation effectiveness of ATRA on Cu surface was evaluated by UV spectroscopy. As shown in Fig. 6, the maximum absorption wavelength was shifted to a lower energy level (redshift) with increased concentration of BTA. This result demonstrates that a part of the added BTA did not make the polymerization reaction with Cu ion, that is, a part of the added BTA was not dissociated with BTA ion and proton at given pH condition, pH 6. However in the case of ATRA, this phenomenon was not observed. Therefore, it was clearly observed that the dissociation tendency of BTA was lower than that of ATRA, which coincided with the results of the pH change shown in Table II.

Static dissolution rate study.— The results of static dissolution rate of Cu according to the amounts of corrosion inhibitor are shown in Fig. 7. Generally, etch rate decreases with increasing corrosion inhibitor concentration. ATRA showed a steady decrease in etch rate

Table I. Changes of anodic current densities according to inhibitor and its concentration.

	BTA		ATRA	
Concentration (M)	Anodic current density (μA/cm²)	Changes (μA/cm²)	Anodic current density (μA/cm²)	Changes (μA/cm²)
0	−727	0	−710	0
0.001	−580	147	−508	202
0.005	−453	274	−309	401
0.01	−247	480	−248	462
0.02	−171	556	−176	534

Table II. Changes of pH of the solution by adding corrosion inhibitors.

	Before addition	After addition
BTA	2.01	2.03
	6.64	5.92
	10.58	7.01
ATRA	2.02	2.04
	6.57	4.24
	10.34	4.56

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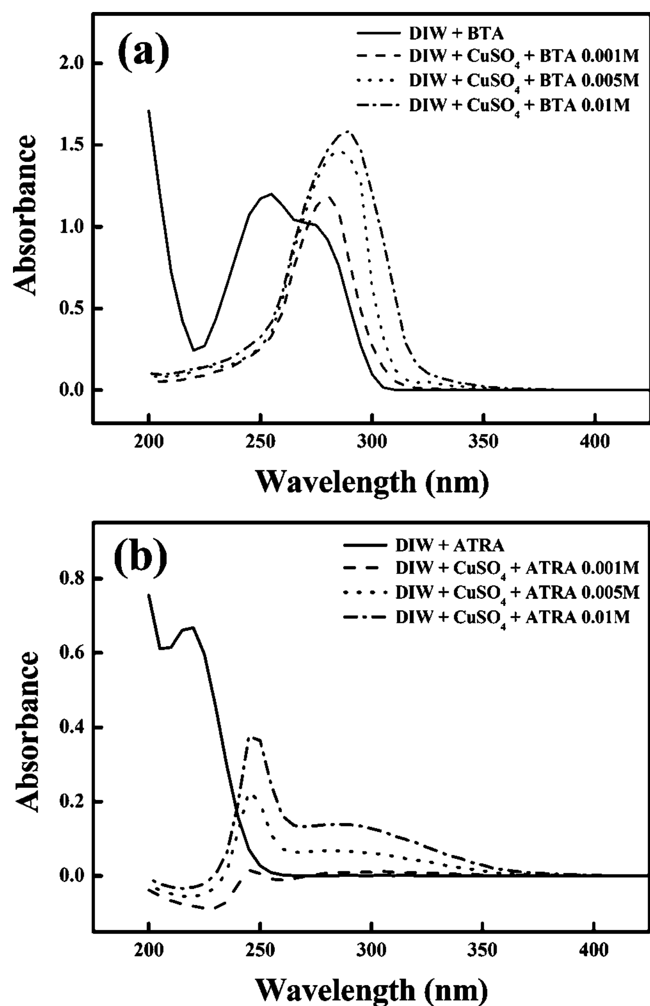

Figure 6. UV-vis spectroscopy analysis results of corrosion inhibitor dissolved in 0.025 M Cu^{2+} ion containing solution from 200 to 1100 nm scan range at pH 6: (a) BTA and (b) ATRA.

with concentration. The addition of BTA, however, resulted in unexpected behavior. An abnormal increase in etch rate was observed

Table III. Structures and specifications of metal patterns.

	#01	#02	#03	#04	#05	#06	#07
Structure							
Size (μm)	400× 400	200×400	100×400	70×400	50×400	30×400	10×400

with 0.001 M and 0.005 M BTA, but the etch rate decreased dramatically to nearly zero at the 0.01 M concentration and seemed to level off as BTA concentrations increased above 0.01 M. From these results, it is assumed that the reaction of BTA with a copper ion is carried out not only by a polymerization reaction with ionic bonding, but also by some other reaction, chelation, and dissolution reaction at 0.001 M and 0.005 M BTA concentration. The studies of BTA as a leveler in Cu electroplating have shown that BTA, which supplies an electron to the cupric ion and transforms the cupric ion to a cuprous ion, accelerates the copper deposition rate at low BTA concentrations.[28-30] This phenomenon indicates that oxidation–reduction reaction of BTA with a copper ion predominates over the polymerization reaction at low concentrations. Therefore, for the case of using BTA in slurry, it is expected that an instantaneous increase in etch rate of Cu will occur with a dilution of BTA concentration during the post-CMP cleaning process.

Chemical mechanical polishing test.— A test module set was manufactured to evaluate the dishing according to the corrosion inhibitors. The test modules are shown in Table III. Each module consisted of a metal line with 100% metal density. The width was varied by 10, 30, 50, 70, 100, 200, and 400 μm.

Figure 8 shows the dishing results, which were measured by a step height profilometer. The depth of dishing increased rapidly at the early stage and was gradually reduced with increasing linewidth. Although the dishing trends of both inhibitors were similar, the differences in dishing were remarkable over 30-μm linewidth and the difference increased with the increase in linewidth, which indicated that the adhesion capability of ATRA on the Cu surface was stronger than that of BTA. In general, total dishing amount is the sum of the local erosion caused by the pad (i.e., bending phenomenon) and the local recess by the chemical reaction. Therefore, ATRA can inhibit the chemical reaction of the oxidizer and reduce the dishing amount more effectively than BTA during the CMP process.

The representative FESEM images of Fig. 9 were taken after a 1000Å SiN layer was deposited for accurate line recess measurement following CMP. While avg 912-Å line recession was measured in BTA, the recession in ATRA was reduced to avg 451Å for line-

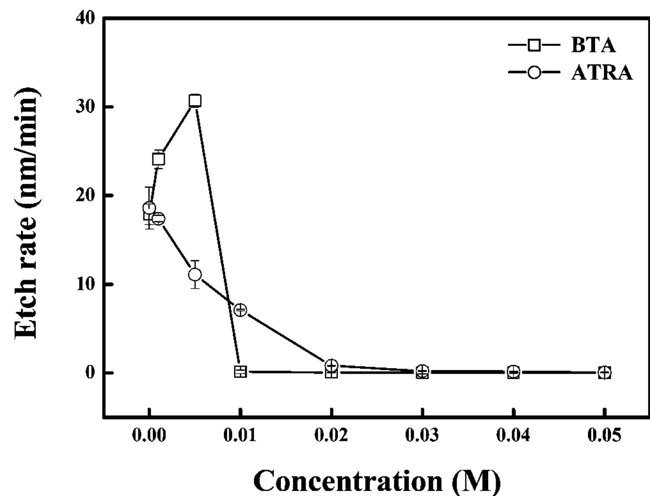

Figure 7. Static etch rate of pure Cu film with increasing concentration of corrosion inhibitor.

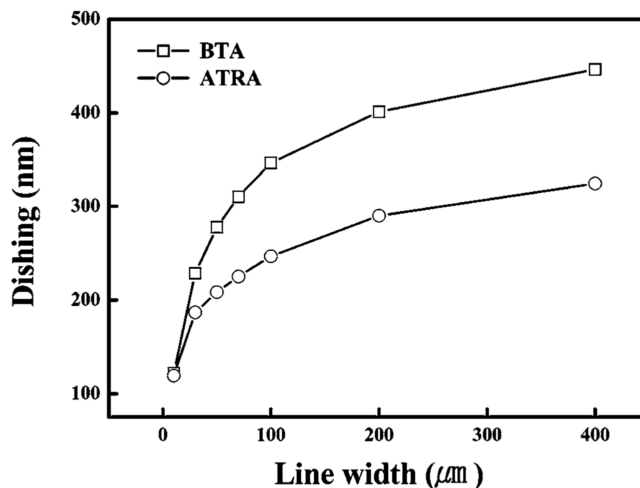

Figure 8. Dishing results measured by step height profilometer (P22) at wide metal line having various widths.

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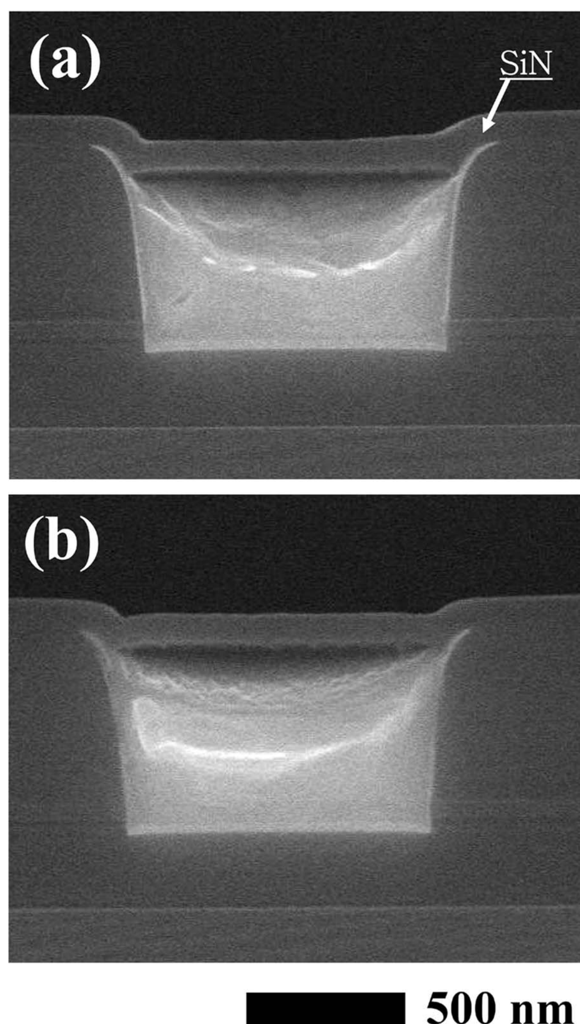

Figure 9. FESEM images of a metal line which has a 1.2 μm linewidth and 0.65 μm height after CMP A 1000-Å SiN was deposited for accurate measurement of line recess: (a) BTA and (b) ATRA.

widths as small as 1 μm. Because a 1-μm linewidth is a region where a pad barely touches during the CMP process, it is inferred that the chemical reaction is mainly responsible for the line recess. Consequently, from the viewpoint of the prevention of chemical reaction, ATRA is more effective than BTA.

Defect review.— Figure 10 shows the surface images of metal lines after CMP. As shown in Fig. 10a, considerable pit corrosion on metal lines after CMP was observed in utilizing BTA inhibitor case only. The pit corrosions were due to the sudden increase of etch rate in diluted BTA concentration by deionized water during the rinsing or cleaning step after polishing. However, as shown in Fig. 10b of using ATRA, pit corrosion was hardly observed, and it was almost same with the result of no additive case.

Conclusions

In this work, the properties and characteristics of BTA and ATRA were evaluated and investigated using various experimental methods. In static etch rate tests, BTA showed unstable and fluctuating results below 0.01 M concentration. From the results of UV-vis spectrometry and FTIR analysis, it was found that ATRA could inhibit metal line corrosion through making a more stable ionic bond with the Cu surface and Cu ion than BTA. Therefore, ATRA showed a more stable static Cu etch rate with concentration. From the viewpoint of the reproducibility of the etch rate, it could be concluded that ATRA was more effective than BTA. Moreover, the effectiveness of ATRA was revealed in the polishing test of patterned wafers. ATRA could form complexes more easily and quickly with a Cu ion than BTA could. The complex compounds of ATRA could be more easily cleaned than those of BTA after polishing due to the simple structure and relatively abundant unpaired electrons of ATRA.

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