



Post-Cu CMP cleaning for colloidal silica abrasive removal

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Abstract

In this study, an efficient approach for the removal of colloidal silica abrasives from the polished copper surface was proposed and demonstrated. This post-chemical mechanical polishing (CMP) cleaning process combines a buffing process with dilute HNO₃/benzotriazole (BTA) aqueous solution for copper surface passivation and a polyvinyl alcohol (PVA) brush scrubbing process with wetting surfactants, Triton X-100, for colloidal silica removal. Buffing with HNO₃/BTA aqueous solution was able to remove copper oxide and form the Cu(I)–BTA hydrophobic passivation. Scrubbing with Triton X-100 surfactant is to enhance the wettability on Cu(I)–BTA surface for the removal of residual silica abrasives. The wetting ability of Triton X-100 was determined by a contact angle and surface tension measurements. It was demonstrated that silica abrasives could be removed efficiently without copper corrosion by this cleaning process.

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1. Introduction

Copper has been accepted as the material for high performance interconnect technology, owing

to its unique electrical properties such as low resistivity and high resistance to electromigration compared with aluminum [1,2]. Since copper is difficult to associate with reactive ion etching (RIE), a Damascene structure has been implemented to realize the copper on-chip interconnects. The Damascene processing utilizes chemical mechanical polishing (CMP) to define the copper interconnect structure. However, this process leaves a large

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amount contamination on the wafer surface, which must be eliminated in the post-CMP cleaning process. The major contaminants include abrasives from slurry, undesired metallic ions and other chemical components [3]. Furthermore, the copper corrosion phenomenon during the post-CMP cleaning process must be prevented [4].

In the copper Damascene process, the CMP procedure is reported to have several stages, i.e., removal of the overburdened copper (out of trench) and Ta/TaN diffusion barrier [5]. During the first stage, overburdened copper with 1–2 μm thickness must be polished at a high rate and stops at the diffusion barrier layer. Sequentially, a non-selective CMP process removes the residual metal (Ta/TaN and Cu) and stops at the SiO_2 dielectric layer, resulting in a flat wafer surface. However, tantalum always spontaneously forms a compact, impervious, and continuous passive oxide (Ta_2O_5) film, which is thermodynamically stable in acidic and alkaline noncomplexing aqueous solutions [6]. Therefore, during the polishing stage of tantalum, a rather low polishing rate of tantalum accompanying longer overpolishing time will lead to a serious dishing and erosion of copper lines. Many researches have been attempted to accomplish a higher polishing rate of tantalum [7–10]. Colloidal silica slurry has been suggested to collocate with H_2O_2 to achieve a higher polishing rate of tantalum. The CMP of tantalum is usually performed using the alkaline aqueous solutions. Babu et al. [8,9] reported that tantalum forms soluble oxotantalate and hydroxotantalate in the presence of H_2O_2 at a high pH value 12. The effect of H_2O_2 in improving the polishing rate of tantalum is mainly owing to enhanced dissociation of peroxide in the alkaline solution. Colloidal silica abrasives with moderately high removal rates, good uniformity values, low defectivity, and excellent ability to remove the tantalum layer are one of the most promising candidates for the copper and tantalum CMP. However, as polishing with colloidal silica based slurry, it shows a strong tendency of the absorption of colloidal silica on the copper surface, which seems to be related to the corrosion of copper and copper oxides formation in the alkaline solution. If H_2O_2 exists, copper tends to be oxidized to form cupric/cupreous ox-

ides (CuO or Cu_2O) and copper hydroxides ($\text{Cu}(\text{OH})_2$) passivation on surface, this may result in the silica abrasives chemisorbed onto this oxide layer by means of the oxygen bridging bonding, as shown in Fig. 1. It is difficult to remove thus chemisorbed colloidal silica by conventional post-CMP cleaning process [3].

In this study, an efficient process for the removal of colloidal silica from the polished copper surface was proposed and demonstrated. This post-CMP cleaning process involves a buffing process on polishing pad with a HNO_3 /benzotriazole (BTA) aqueous solution (abrasive free) for copper surface passivation and a polyvinyl alcohol (PVA) brush scrubbing process with a wetting

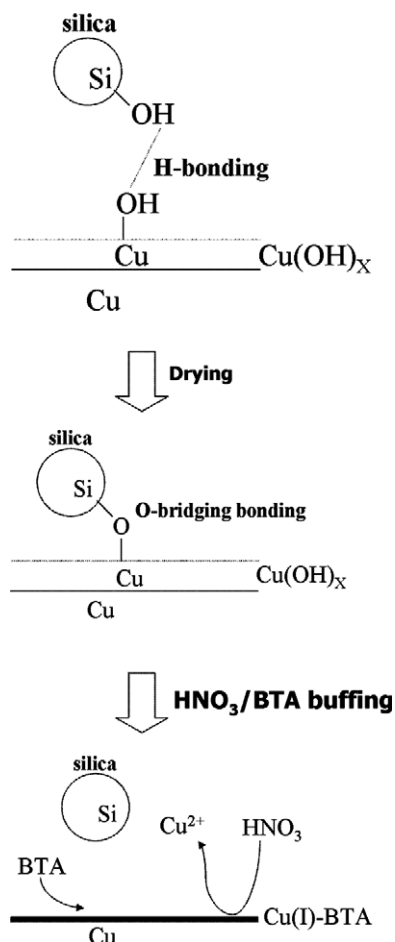


Fig. 1. Schematic illustration of the removal of colloidal silica abrasive by the HNO_3 /BTA buffing process.

surfactants, Triton X-100 ($C(CH_3)_3CH_2C(CH_3)_2-C_6H_4(OCH_2CH_2)_{10}OH$), for colloidal silica removal. In the buffing process, HNO_3 dissolves the surface copper oxide passivation, and Cu^+ ions would coordinate with BTA to form a mono-layer of Cu(I)–BTA on the surface to prevent further copper oxide formation (see Fig. 1). However, the Cu(I)–BTA surface is basically a hydrophobic surface, which promotes the re-adsorption of colloidal silica onto the Cu(I)–BTA surface. Therefore, a scrubbing process with the cleaning solution containing Triton X-100 surfactant is utilized to modify the wettability of the Cu(I)–BTA surface and remove the residual silica abrasives after the HNO_3 /BTA buffing process. We demonstrated that the chemisorbed colloidal silica abrasives could be removed effectively by the cleaning process without copper corrosion phenomenon.

2. Experimental

2.1. Preparation of patterned wafers

CMP and post-CMP cleaning experiments were performed utilizing p-type, (100) oriented, 6-in. silicon wafers. The patterned wafers were prepared first by thermally growing about 800 nm thick of SiO_2 on the silicon substrate in furnace after the standard RCA cleaning. The desired metal pattern was transferred into the SiO_2 layer by means of g-line optical lithography and RIE. The trenches were etched to a depth of 800 nm. The wafers were then deposited with a 50 nm thick layer of sputtered tantalum, followed by a 1700 nm thick copper film by electroplating.

2.2. CMP and post-CMP cleaning

The polishing process was performed on a polisher (IPEC/Westech 372M) with colloidal silica based slurry (Bayer 50ck) on the embossed pad (RODEL Politex Regular™). The slurry formulation consists of 10 wt% colloidal silica and 10 vol% H_2O_2 . The polishing parameters, such as down force, back pressure, platen and carrier rotation speeds, and slurry flow rate, were set to be 5, 2

psi, at 42, 45 rpm for 150 ml/min, respectively. After polishing, the test wafers were buffed with the HNO_3 /BTA aqueous (abrasive free) solution on the same polishing pad and polishing parameters. Subsequently, the polished wafers were cleaned on a PVA brush cleaner (SSEC-M50) with the Triton X-100 cleaning solution. Each of the test wafers must be processed by cleaner immediately after polishing to avoid slurry drying. Field-emission scanning electron microscopy (FE-SEM, HITACHI S-4000) and atom force microscopy (AFM, DI-5000) were used to determine the cleaning performance.

2.3. Wetting ability of Triton-X 100

The wetting ability of Triton X-100 on the Cu(I)–BTA surface was investigated by the contact angle experiment. Blanket copper coated wafers were first immersed in a HNO_3 /BTA solution and briefly rinsed with DI water to form a Cu(I)–BTA mono-layer on the copper surface. The wetting ability of Triton X-100 on the Cu(I)–BTA surface was then determined on a contact angle meter using DI water and Triton X-100 solution.

A drop-weight method was used to determine the surface tension (γ) of Triton X-100 solution [11]. Drops of the solution were allowed to detach themselves slowly from the tip of a vertically mounted narrow tube and their weight was measured. The surface tension of solution (γ_L) was given by

$$\gamma_L = \frac{\Phi mg}{2\pi r}, \quad (1)$$

where m is the mass of the drop, r is the radius of the tube and Φ is a correction factor.

3. Results and discussion

Fig. 2 shows the side-view FE-SEM image of the Cu/ SiO_2 Damascene interconnection structure after polishing with colloidal silica based slurry and DI water rinse. It is obvious that a lot of colloidal silica abrasives still remain on the wafer surface and adsorb selectively on the copper surface, rather than SiO_2 surface. For the SiO_2 interlayer

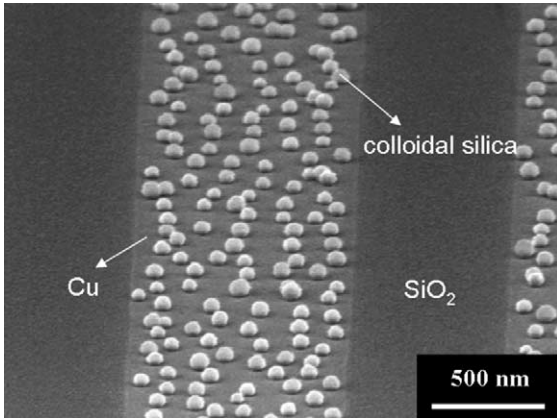


Fig. 2. Side-view FE-SEM image of the Cu/SiO₂ Damascene interconnection structure after polishing with colloidal silica based slurry and DI water rinse.

dielectric (ILD) surface in aqueous solution, both SiO₂ surface and colloidal silica will possess same sign of surface zeta potential (iso-electric point of SiO₂ ~ 2.2) [12], therefore, an electrostatic repulsion force exists between the colloidal silica and the hydrophilic SiO₂ surface, resulting in the desorption of the silica particles. For copper surface, after polishing with colloidal silica, there is an oxygen bridging bonding between the colloidal silica and the surface cupric/cuprous oxides.

Therefore, the colloidal silica tends to be chemisorbed onto the copper surface and becomes difficult to be removed. Fig. 3 shows the AFM images of the polished copper surface after DI water rinse. It is clear that significant amount of colloidal silica remains on the copper surface. In order to effectively remove the colloidal silica from the copper surface, it is necessary to break the chemical bonding between the colloidal silica and the copper oxides.

3.1. Removal of chemisorbed colloidal silica abrasives by HNO₃/BTA buffing

In this study, a buffing process with HNO₃/BTA chemistry was first introduced to remove the colloidal silica abrasives from the polished copper surface. During the HNO₃/BTA buffing process, HNO₃ etches a thin surface layer of copper oxides and releases the attached colloidal silica. BTA is a well known copper corrosion inhibitor, which forms a Cu(I)–BTA passivation to protect the underlying copper from copper oxides formation. Because the polished copper oxides surface is replaced by the Cu(I)–BTA passivation, the chemisorbed silica abrasives is expected to be released.

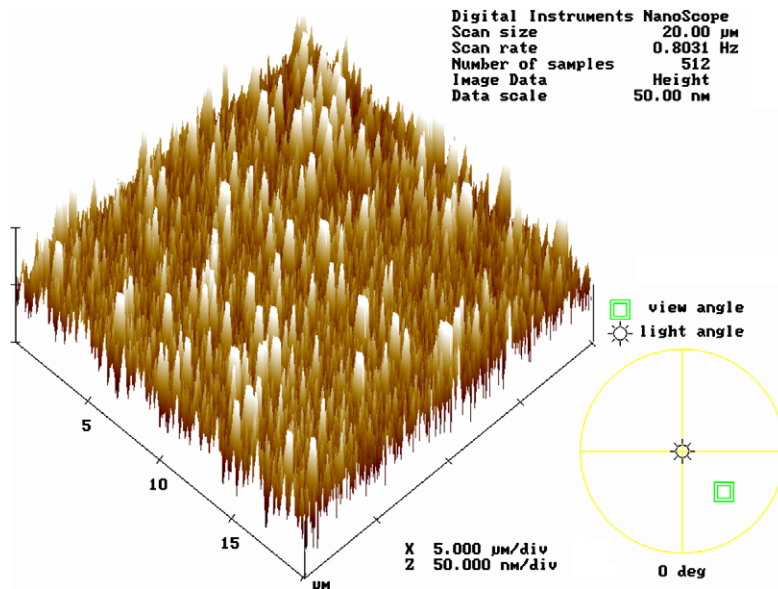


Fig. 3. AFM image of the Cu surface after polishing with colloidal silica based slurry and DI water rinse.

Fig. 4(a) shows the AFM images of the polished copper surface after buffing with 3 vol% HNO_3 /0.001 M BTA aqueous solution for 60 s. After buffing, a significant removal of colloidal silica is achieved, compared with the DI water rinse (see Fig. 3). It is, therefore, suggested that the Cu(I)–BTA passivation formed on the copper surface will protect copper from the oxygen bridged bonding with colloidal silica, provided long immersion in HNO_3 /BTA aqueous solution (60 s). However, a thin copper layer, about 100 nm in thickness, was etched away during this buffing condition. It is unfortunate that the dishing phenomenon of copper lines caused by CMP process will be deteriorated. There are two ways to diminish the removal of copper during the HNO_3 /BTA buffing

process, namely increase of the BTA concentration and decrease of the buffing time.

In order to minimize the copper dishing, buffing with higher BAT concentration was carried out. In the case of buffing with 3 vol% HNO_3 /0.005 M BTA aqueous for 60 s, the removal of copper is reduced to about 50 nm while the colloidal silica is cleaned as well (see Fig. 4(b)). As the BTA concentration is increased to 0.01 M, Fig. 4(c) shows that the removal of colloidal silica by buffing is relatively poor. This result may be related to that the Cu(I)–BTA layer formation rate is higher for buffing at higher BTA concentration. If the Cu(I)–BTA passivation formation rate is higher then the copper oxide etching rate, BTA can also adsorb on the copper oxides surface [13] and inhibits

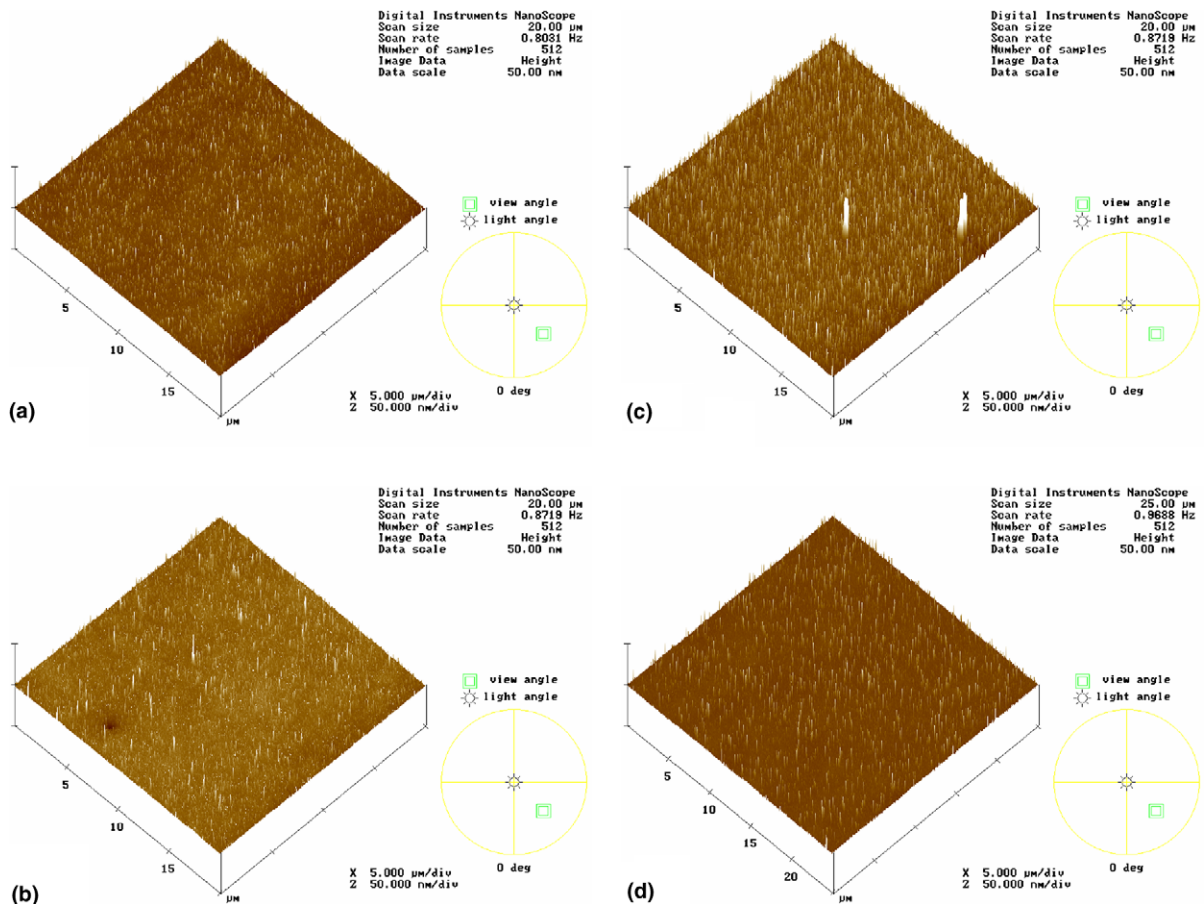


Fig. 4. AFM images of the polished Cu surface after: (a) buffing with 3 vol% HNO_3 /0.001 M BTA for 60 s; (b) 3 vol% HNO_3 /0.005 M BTA for 60 s; (c) 3 vol% HNO_3 /0.01 M BTA for 60 s; (d) 3 vol% HNO_3 /0.005 M BTA for 10 s.

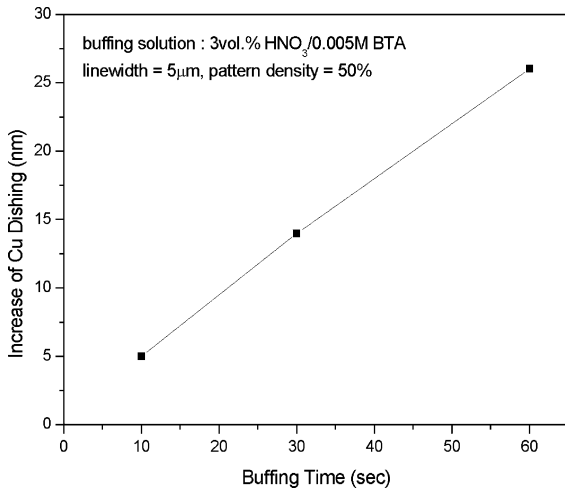


Fig. 5. Increase amount of Cu dishing after buffing with 3 vol.% $\text{HNO}_3/0.005 \text{ M BTA}$ aqueous as a function of buffing time.

the further etching of the oxide layer. Therefore, colloidal silica still remains on the copper oxide surface after buffing with higher BTA concentration (0.01 M).

In order to minimize the removal of copper while maintaining a high removal of colloidal silica during the buffing process, the effect of buffing time on buffing performance was investigated. Fig. 5 illustrates the increase amount of copper dishing after buffing with 3 vol.% $\text{HNO}_3/0.005 \text{ M BTA}$ aqueous as a function of buffing time. The results show that the copper dishing decreases with decreasing buffing time. For the patterned wafer buffed only for 10 s, the dishing amount of copper lines is only about 5 nm. The cleaning performance of the buffing condition (see Fig. 4(d)) is similar to that of buffing for 60 s (see Fig. 4(b)). These results suggest that the BTA concentration plays an important role in gaining optima cleaning performance and a suitable buffing time is necessary for minimizing the copper dishing.

3.2. Removal of chemisorbed colloidal silica abrasives by PVA brushing with surfactant

Although the HNO_3/BTA buffing process can remove the colloidal silica abrasives effectively,

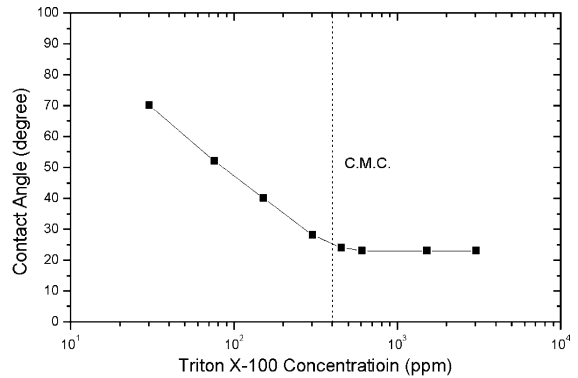


Fig. 6. Effect of Triton X-100 concentration on the contact angle of Triton X-100 solution with Cu(I)-BTA surface.

Fig. 4 shows that few particles still remain on the copper surface, since the Cu(I)-BTA surface is typically hydrophobic. Experiment showed that the contact angle of water drop on the Cu(I)-BTA surface is about 90° . Therefore, the colloidal silica abrasives will tend to re-adsorb onto the hydrophobic Cu(I)-BTA surface, possibly due to the van der Waals attraction. In this study, a PVA brush scrubbing with nonionic surfactant, Triton X-100, which was introduced to increase the wettability the Cu(I)-BTA surface and enhance the removal of residual colloidal silica after the buffing process. Triton X-100 was chosen due to its nonionic nature, since it is not desirable to introduce additional ionic contamination in the wafer cleaning process.

Removal of particulate solid from a surface can be accomplished by wetting of the substrate and the solid particles by aqueous bath. For all the wetting processes, reduction of the interfacial tension between substrate and the wetting liquid, γ_{SL} , is beneficial, but that reduction of the surface tension of the liquid, γ_{L} , per se is not always of benefit [14]. Fig. 6 shows the contact angle of the Triton X-100 solution drops of various concentration on the Cu(I)-BTA surface. The results indicate that the contact angle on the Cu(I)-BTA surface decreases with increasing Triton X-100 concentration, until the critical micelle concentration (CMC) of Triton X-100 (about 400 ppm). The decrease of contact angle can be attributed to two

reasons, namely the adsorption of surfactant at solid/liquid interface and the decrease of solution surface tension. The adsorption of surfactant at the solid–liquid interfaces lowers the surface tension (γ_{SL}). On the other hand, adsorption at the vapor–liquid interface with the consequent lowering of γ_L and foaming is not suitable for being wetting agents. Therefore, the γ_{SL} of Cu(I)–BTA surface and Triton X-100 bath solution interface was investigated to demonstrate the wetting ability of Triton X-100.

The tendency of a liquid phase to spread over the substrate surface can be given by the spreading coefficient, $S_{L/S} = \gamma_S - \gamma_{SL} - \gamma_L$. If the spreading coefficient is positive then spreading occurs spontaneously; if not, mechanical work must be done to wet the surface completely [14]. In order to determine the γ_{SL} , the γ_L of Triton X-100 solution and the γ_S of Cu(I)–BTA surface were first determined by a drop-weight method and the Girifalco–Good–Fowkes–Young equation (Eq. (2)),

respectively. Then, the γ_{SL} of Cu(I)–BTA surface and Triton X-100 solution interface is acquired by the Young’s equation (Eq. (3)).

$$\cos \theta = -1 + \frac{2(\gamma_S \gamma_W^d)^{1/2}}{\gamma_W}, \tag{2}$$

$$\gamma_{SL} + \gamma_L \cos \theta - \gamma_S = 0, \tag{3}$$

where θ is the contact angle, γ_W is the surface tension of water (about 72.8 mN/m), γ_W^d is the dispersion force of water (about 21 mN/m). From contact angle measurement, the surface tension of Cu(I)–BTA surface, γ_S , is about 63 mN/m. Fig. 7 shows the γ_{SL} and γ_L as a function of the Triton X-100 concentration. For pure water phase, the value of spreading coefficient is about -72.8 mN/m (see Table 1). As the Triton X-100 concentration increases, the spreading coefficient decreases continuously. From these results, it is concluded that Triton X-100 shows good wetting ability for the Cu(I)–BTA surface. The Triton X-100 molecule can adsorb on the hydrophobic Cu(I)–BTA surface effectively and lower the γ_{SL} , therefore, the Cu(I)–BTA surface changes to hydrophilic sequentially.

Since the spreading coefficient between Triton X-100 bath solution and Cu(I)–BTA surface is negative (see Table 1), mechanical work must be done to wet the surface completely. In this study, a PVA brush scrubbing process with the Triton X-100 solution is proposed to clean the residual colloidal silica after the HNO₃/BTA buffing process. In the PVA brush scrubbing test, the polished blanket and patterned wafers were first buffed with 3 vol% HNO₃/0.005 M BTA aqueous for 10 s, then, scrubbed with 400 ppm Triton X-100 solu-

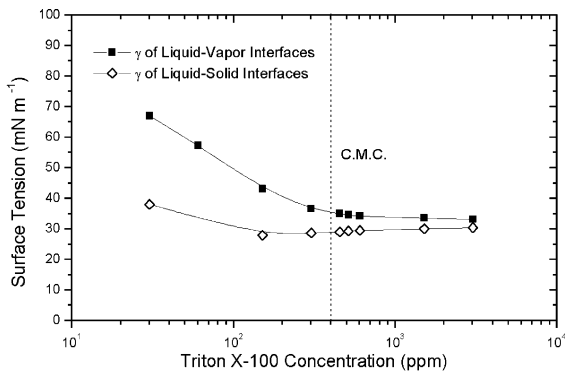


Fig. 7. γ_{SL} and γ_L as a function of the Triton X-100 concentration.

Table 1

Summary of the experimental and calculated results for the surface tension (γ) and spreading coefficient ($S_{L/S}$) at various concentrations of Triton X-100

Triton X-100 concentration (ppm)	0 ^a	30.4	60.8	151.9	303.7	400	455.6	516.4	607.5	1518.7	3037.3
γ_S (mN/m)	63	63	63	63	63	63	63	63	63	63	63
γ_{SL} (mN/m)	63	37.9	34	27.8	28.6	30	28.9	29.3	29.4	29.9	30.3
γ_L (mN/m)	72.8	66.8	57.2	43	36.5	35	34.9	34.5	34.1	33.5	33.1
$S_{L/S}$ (mN/m) ^b	-72.8	-47.7	-28.2	-7.8	-2.1	-2	-0.8	-0.8	-0.5	-0.4	-0.4

^a DI water.

^b $S_{L/S} = \gamma_S - \gamma_{SL} - \gamma_L$.

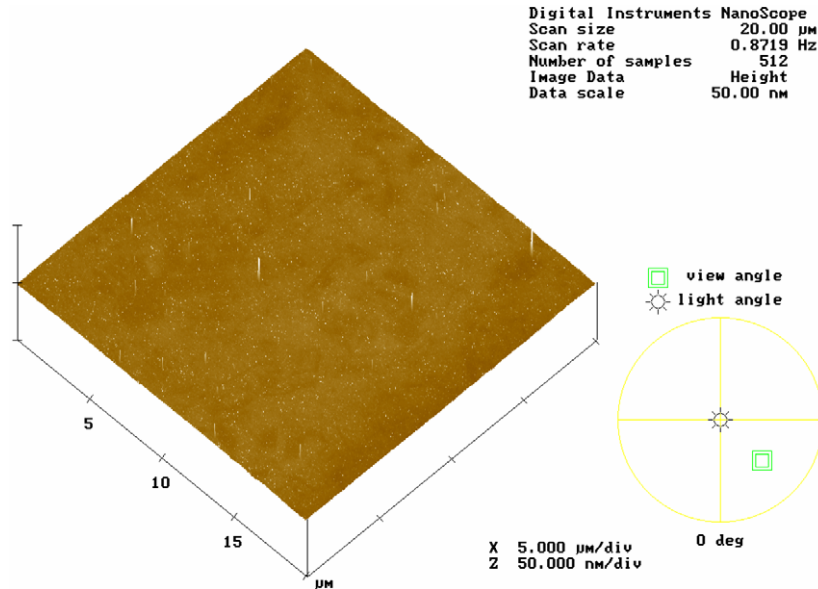


Fig. 8. AFM image of the polished Cu surface after buffing with 3 vol% HNO_3 /0.005 M BTA aqueous for 10 s and scrubbing with 400 ppm of Triton X-100 solution.

tion (CMC). From the contact angle and the surface tension measurements, it is found that in the Triton X-100 bath solution with CMC level, the γ_{SL} and γ_{L} decrease to the value about 30 mN/m and 35 mN/m (see Fig. 7), respectively, and the spreading coefficient is about -2 mN/m (see Table 1). Apparently, the reduction of spreading coefficient is caused by adsorption of surfactant molecules onto the Cu(I)–BTA surface with their hydrophilic groups oriented toward the bath and the reduced van der Waals attraction resulting from hydration of these hydrophilic groups. The AFM image of copper surface after the suggested post-CMP cleaning is shown in Fig. 8. As shown, a very clean and smooth copper surface is observed. Fig. 9 shows the side-view FE-SEM image of the Cu/SiO₂ Damascene interconnection structure after CMP and post-CMP cleaning. It is obvious that the adsorbed colloidal silica abrasives are removed significantly, resulting in a clean wafer surface. Because the Cu(I)–BTA surface turns to be hydrophilic after this scrubbing process, the colloidal silica can be carried away in the effluent on the full rinsed Cu(I)–BTA surface. Since the adsorption of nonionic surfactant does not signif-

icantly increase the electrical potential at the Stern layer, it appears that steric barriers is the major mechanism for the prevention of particulate redeposition. Furthermore, the post-CMP cleaning process do not appear to corrode the polished copper surface, which is one major issue to utilize the process for the copper CMP cleaning successfully.

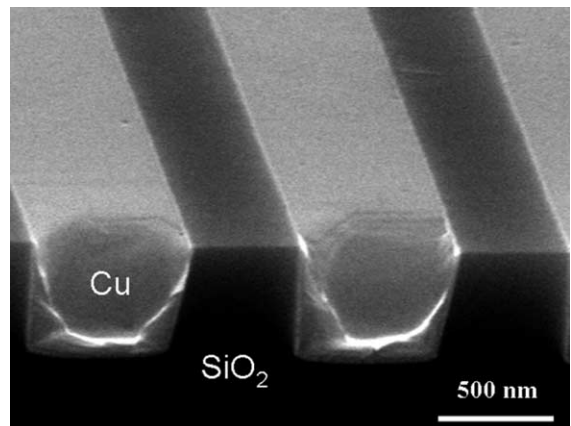


Fig. 9. Side-view FE-SEM image of the Cu/SiO₂ Damascene interconnection structure after CMP and post-CMP cleaning.

4. Conclusions

In this study, a novel cleaning process, based on the HNO₃/BTA buffing and the PVA brush scrubbing with nonionic surfactant, Triton X-100, were developed to remove the colloidal silica abrasives from the CMP-polished copper surface. It shows good colloidal silica removal ability by buffing with the HNO₃/BTA aqueous solution, although the buffing process will lead to the deterioration of copper dishing. By adjusting the BTA concentration and buffing time, the optima buffing performance can be obtained and amount of copper lines dishing can be minimized. After buffing, the Cu(I)-BTA surface is basically hydrophobic, on which silica may re-adsorb. In order to remove residual colloidal silica completely, a PVA brush scrubbing process with Triton X-100 solution was introduced after buffing process. We have shown that a clean and smooth copper surface was obtained after cleaning process.

Acknowledgements

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