

TiN metal hardmask etch residue removal on advanced porous low-k and Cu device with corner rounding scheme

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Keywords: Metal hardmask, etch residues removals, sidewall polymer, TiN etch, Cu/low-k

Abstract. A novel wet cleaning formulation approach was developed with a TiN etch rate of more than 30 Å/min at room temperature and more than 100 Å/min at 50°C. The chemicals are compatible with Cu and low-k materials, and are suitable for Cu dual damascene interconnect 28 nm and smaller technology node applications. The chemicals offer a route to *in situ* controlled TiN pullback or even complete removal of the TiN mask during the cleaning process in single wafer tool applications. The chemicals do not contain NH₄OH or TMAH and so are very user-friendly.

Introduction

Plasma dry etch processes are commonly used to fabricate vertical sidewall trenches and anisotropic interconnecting vias for copper (Cu) / low-k dual damascene devices. As the technology nodes advance to 45nm and smaller, the decreasing size of semiconductor devices makes achieving critical profile control of vias and trenches more challenging. IC companies are investigating the use of metal hardmasks to improve etch selectivity to low-k materials and thereby gain better profile control. In order to obtain high yield and low-resistance interconnects, the polymers on the sidewalls and the particulate/polymer residues at the via bottoms that are generated during etching must be removed prior to the next process step. It would be beneficial if the cleaning solution is also able to etch the TiN hardmask to form pulled-back/rounded corner morphology. This would prevent bowing of the low-k or undercutting of the hardmask, enabling reliable deposition of barrier metal, Cu seed layer and Cu filling. Taking this concept one step further and fully removing the metal hardmask could offer numerous benefits to down stream processes, particularly CMP, by eliminating the need for barrier CMP. To realize either goal, the cleaning solution must be compatible to both low-k and Cu while simultaneously able to remove all etch by-products and residues.

Many approaches to removing these etch residues have been explored [1-5]. Research on TiN etching with ammonium hydroxide-hydrogen peroxide-water mixtures, and tetramethylammonium hydroxide (TMAH) - hydrogen peroxide-water mixtures have been conducted [6-9]. An etch rate selectivity of less than 10 for TiN towards Cu has also been reported [6]. A selectivity higher than 10 is required to achieve a TiN pull-back/rounded corner scheme while simultaneously maintaining compatibility with Cu. In this paper, we report a recently-developed, novel wet cleaning formulation approach. By incorporating a novel Cu corrosion inhibitor and a novel TiN etch enhancement chemical (herein referred to as “compound A”) in our formulation, we are able to achieve (i) high TiN/Cu etch rate selectivity (ii) completely etch residue removal, (iii) compatibility with low-k and Cu, (iv) the ability to tune performance to provide either TiN pullback/corner rounding or to completely remove TiN and (v) suitability for single wafer tool applications.

Experiments

The residue removal experiments were conducted in beakers at room temperature, 30°, 40° and 50°C for various times. The TiN and Cu etch rate experiments were also conducted at room temperature, 30°, 40° and 50°C for 10 minutes each. The residue removal efficiency was evaluated

from SEM results (Hitachi S-5500) in the areas of etched sidewalls, via bottoms and on the tops of the wafer samples, as shown in Figure 2. The TiN and Cu thicknesses were measured using a Four Dimensions Four Point Probe Meter 333A, whereby the resistivity of the composition is correlated to the thickness of the film remaining. The TEOS and low-k materials thickness were measured using a KLA-Tencor SM300 instrument. The etch rate was calculated as the thickness change (before and after chemical treatment) divided by the chemical treatment time. Chemical solution pH was measured with a Beckman 260 pH/Temp/mV meter. The H₂O₂ used in these experiments was semiconductor grade PURANAL (Aldrich 40267).

Results and discussion

Figure 1 shows a wafer with residues after dry etching using a TiN etching mask. Figure 2 shows the complete removal of the etching residues and TiN etch mask after treatment with HCX-T002C-A at 50°C for 2 mins. The TiN etch rate increases with process temperature as shown in Table I. The TiN pullback at 30° and 40°C for 2 mins, respectively for HCX-T002C-A are shown in Figure 3. The TiN mask pullback become more pronounced as the TiN etch rate is increased (by increasing process temp from 30° to 40°C). The same TiN pullback morphology is seen in Figure 4 for HCX-T002C-C; the TiN pullback is more significant at 30°C than at room temperature. Table 1 highlights the low impact of HCX-T002C on low-k and TEOS dielectrics.

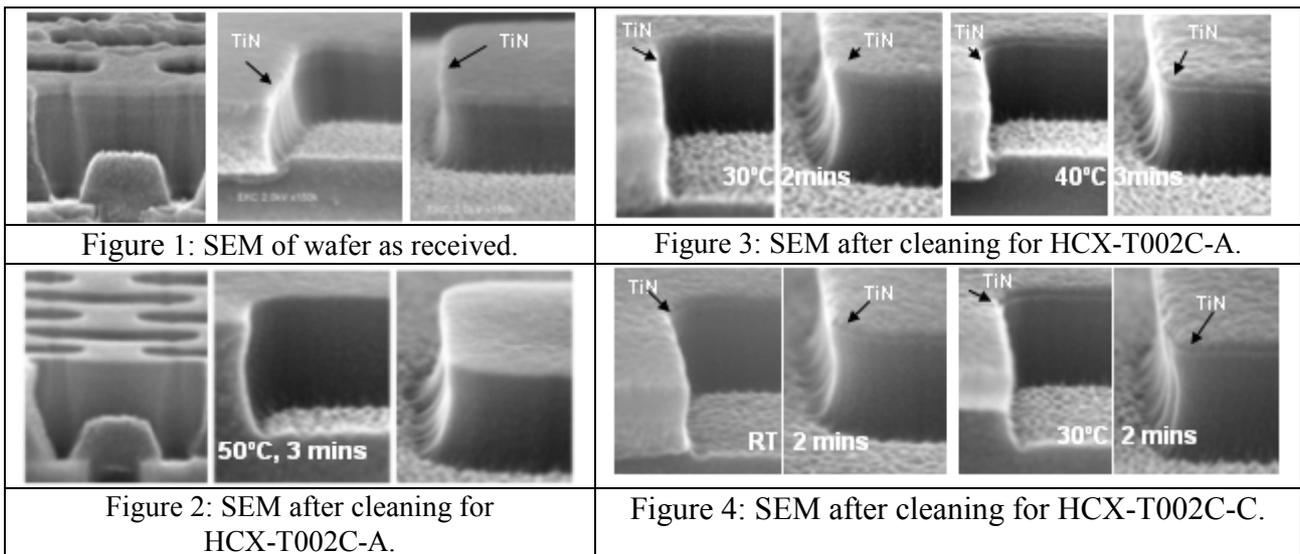


Table I: The etch rate for various materials.

Chemical	Temperature(°C)	Cu (Å/min)	TiN (Å/min)	TEOS (Å/min)	Low-K(BDII) (Å/min)
HCX-T002C-A	30	0.43	30.5	0.75	0.90
	40	1.19	68	-1.05	0.4
	50	1.89	>100	-0.1	0.39
HCX-T002C- B	30	1.7	40	0.5	0.65
HCX-T002C- C	22(RT)	1.6	29.65	0.15	0.50
	30	1.9	50	0.35	0.49

Figure 5 shows the TiN and Cu etch rates vs. pH change at 30°C. The TiN etch rate increases with increasing pH because the TiN etch rate is directly related to HO₂⁻ species concentration [9]. As the pH increases, the concentration of HO₂⁻ also increases, resulting in a higher TiN etch rate. Figure 5 also shows that the TiN etch rate can be tuned by simply changing chemical pH. It is important to keep pH constant during the chemical cleaning process in order to obtain constant TiN

etch rate while maintaining H_2O_2 concentration unchanged. The Cu etch rate remains very low ($<2 \text{ \AA}/\text{min}$) between pH 6.0 and 9.3 due to the presence of the Cu corrosion inhibitor which prevents Cu from being oxidized and removed within that pH range.

Figure 6 shows that the TiN etch rate is increased with increasing H_2O_2 concentration at 30°C and pH 9.2. Higher concentrations of H_2O_2 result in higher concentrations of the HO_2^- species, which is the primary active species in TiN etching [9]. Thus the TiN etch rate increases with increasing H_2O_2 concentration. If complete removal of the hardmask is preferred, one option is to use a high concentration of H_2O_2 in the cleaning formulation.

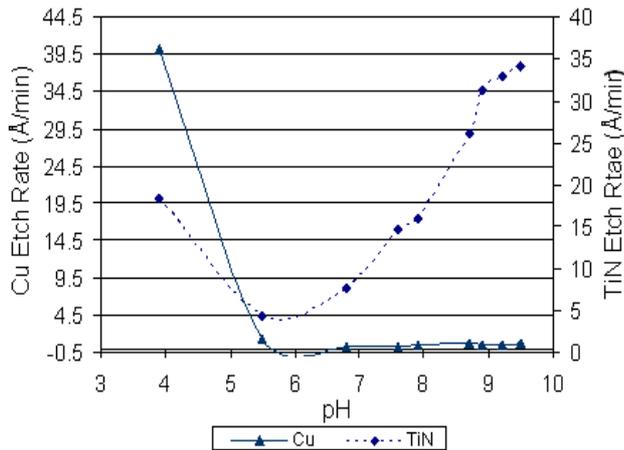


Figure 5: TiN and Cu etch rate vs. pH at 30°C .

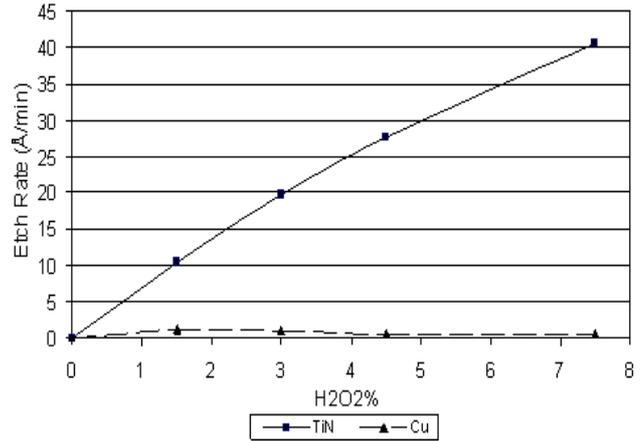


Figure 6: TiN and Cu etch rate vs. H_2O_2 % at 30°C (pH: 9.2).

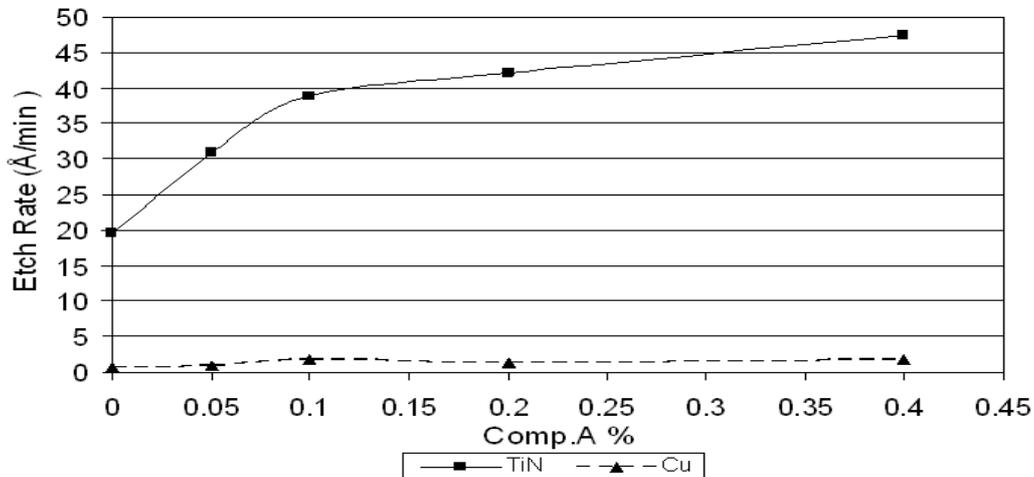


Figure 7: TiN and Cu etch rate vs. comp. A% at 30°C (H_2O_2 fixed, pH: 9.3).

Figure 7 shows that the TiN etch rate at 30°C is increased with “compound A” concentration. In the absence of “compound A” the TiN etch rate is about $20 \text{ \AA}/\text{min}$. With 0.1% “compound A” in the formulation the TiN etch rate is nearly doubled. A formulation with an inherently high TiN etching rate enables low temperature processes. A low temperature process has a reduced H_2O_2 decomposition rate [10], which consequently extends the formulation bath life. Figure 7 shows that Cu etch rate is very low -- less than $2 \text{ \AA}/\text{min}$. “Compound A” has no impact on Cu etch rate in the formulations.

TiN and Cu etch rates of HXC-T002C-A, HXC-T002C-B and HXC-T002C-C are provided in Table 1. HXC-T002C-B contains a slightly higher “compound A” concentration than HXC-T002C-A does. As a result, at 30°C HXC-T002C-B shows a TiN etch rate of $40 \text{ \AA}/\text{min}$ vs. $30 \text{ \AA}/\text{min}$ for HXC-T002C-A. HXC-T002C-C has a slightly higher H_2O_2 concentration (increased by less than

1.6 %) compared with HCX-T002C-B; at 30°C HCX-T002C-C delivers a TiN etch rate of 50 Å/min vs. 40 Å/min for HCX-T002C-B. HCX-T002C-C also delivers a 30Å/min TiN etching at room temperature (22°C). Table I shows that all formulations are Cu-compatible at the temperatures tested. In summary, “compound A” and H₂O₂ concentration can be used to tune the formulation for a high TiN etch rate, which in turn enables low temperature processing and improved bath life.

HCX-T002C has been qualified for cleaning 28nm node Cu dual damascene TiN Metal hardmask interconnects on a single wafer platform with a major IC manufacturer. The chemical is verified as compatible with low-k, and shows excellent cleaning and electrical functional performance on metal-line and via chain yields (WAT), EM and TDDDB test results. The performance exceeds that of dilute HF cleaning in every test mentioned. At present, the customer has adopted this HCX-T002C as their benchmark cleaning product in the fabrication facility.

Summary

A series of formulations with highly selective removal of TiN over Cu and low-k have been successfully developed and comprehensively tested in Fab. Compound A has been shown to enhance TiN etch rates in conjunction with H₂O₂. By introducing a novel Cu corrosion inhibitor, the oxidation and subsequent corrosion of Cu by H₂O₂ can be prevented. For a given subset of formulation components, it has been demonstrated that the etch rate selectivity between TiN and Cu can be further controlled and tuned by pH and/or process conditions while still being able to maintain full compatibility to Cu and low-k. Complete removal of post etch residues was also achieved using these cleaning solutions. One of these formulations has been qualified for 28nm node manufacture at a major IC Fab. Importantly, these formulations also offer a route to controlled pullback or even the complete removal of TiN masks *in situ* during cleaning. This, in turn, presents potential benefits during subsequent metal deposition processes and eliminates the need for barrier CMP and subsequent post-CMP cleaning steps, thus enhancing overall device fabrication yields.

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Ultra Clean Processing of Semiconductor Surfaces X

10.4028/www.scientific.net/SSP.187

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10.4028/www.scientific.net/SSP.187.241