TiN Metal Hardmask Etch Residue Removal with Mask Pullback and Complete Mask Removal for Cu Dual Damascene Device

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Abstract— **Formulations with TiN/Cu etch rate selectivity greater than 60 at 40 °C for TiN pullback and 200 at 55° C for complete TiN mask removal, respectively, have been developed. The formulations are compatible with Cu, low-k and SiON materials, and prevent Cu re-oxidation.**

Keywords: Etch residue removal, TiN Metal hardmask, Cu/low-k, single wafer cleaning, TiN etch

I. INTRODUCTION

IC companies use TiN as a reactive-ion etching (RIE) hardmask to achieve improved selectivity to low-k materials in Cu dual damascene device fabrication for the 32 nm node and beyond. However, a disadvantage with this approach is that an overhang mask is produced after RIE, which could result in voids in the subsequent deposition steps of barrier metal, Cu seed layer and Cu filling. Therefore, it is beneficial to etch the TiN mask in such a way as to form a pullback/rounded corner morphology to eliminate mask overhang and ensure reliable metal deposition. For technology nodes 20nm and beyond it is more desirable to completely remove the TiN hardmask to reduce the aspect ratio of etched structures for better subsequent metal deposition of barrier metal, Cu seed layer and Cu filling. Thus, a post-etching residue cleaner is required to simultaneously remove all post etch residues and etch TiN to create pullback, or completely remove the TiN mask. In addition, the cleaning solution must remove CuO_x and prevent re-oxidation of Cu and must be compatible with low-k, TEOS and Cu materials.

In this paper we report a recently-developed wet cleaning formulation approach. By incorporating a novel Cu corrosion inhibitor and an oxidizer in the formulation, we are able to achieve a TiN/Cu etch rate selectivity of greater than 60, and the formulation (i) removes all etch residues, (ii) is compatible with low-k, TEOS, Cu and Co, (iii) etches TiN to provide pullback/corner rounded morphology and (iv) is able to remove CuO_x and prevent Cu oxidation during and after cleaning. By incorporating novel TiN etch enhancement chemicals (herein referred to as “compound A” and “compound B”) in the formulation, TiN/Cu etch rate selectivity of more than 200 is achieved for applications requiring complete TiN mask removal.

II. EXPERIMENTS

Residue removal experiments were conducted in beakers at 45ºC for 2 minutes. 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.

The Co etch rate experiments were conducted at 30 °C and 40 ºC and Cu experiments were at 30 ºC, 40 ºC and 55 ºC; each experiment was 10 minutes in duration. TiN etch rate experiments were conducted at 30 °C for 10 minutes, 40 ºC for 7 minutes and 55 ºC for 5 minutes. The etch rates were calculated as the difference in thickness, before and after, divided by the chemical treatment time. The TiN, Co and Cu thicknesses were measured using a Four Point Probe Meter 333A. The TEOS, low-k and SiON etch rate experiments were conducted at 30 °C, 46 ºC and 55 ºC for 10 minutes each. The TEOS thickness was measured with KLA-Tenor SM300. Low-k and SiON material thicknesses were measured with Auto SE Spectroscopic Ellipsometer by HORIBA JOBIN YVON.

The hydrogen peroxide used for HCX-T002C formulation was semiconductor grade PURANAL (Aldrich 40267), and semiconductor grade hydrogen peroxide by VWR (JT2190-3) was used for the HCX35 series formulation study.

The test for Cu oxidation barrier functionality was conducted by first removing CuOx from Cu blank wafer pieces with an in-house procedure. Then the Cu wafer pieces were treated with the experimental product under study: HCX-T002C at 50 ºC, HCX35 at 55 ºC or HCX35-1 at 55 ºC, each for 2 minutes followed by a 5 minute deionized water (DIW) rinse and dry. Another Cu blank wafer piece with CuOx removed was used as a control, with the only treatment being a 5 min DIW rinse and dry. SEM was used to examine the CuOx growth on all three Cu blank wafer pieces.

III. RESULTS AND DISCUSSION

Fig. 1 shows that the TiN etch rate is increased with increasing H_2O_2 concentration at 30 ºC and pH 9.2. In the absence of hydrogen peroxide the TiN etch rate is zero. H_2O_2 is used to oxidize TiN to permit removal of TiN. The low Cu etch rate (<2 Å/min) shown in Fig. 1 is due to the presence of the Cu corrosion inhibitor which prevents Cu from being oxidized and subsequently removed during the process. Fig. 2 shows that the TiN etch rate is increased with "compound A" concentration at 45 ºC. In the absence of "compound A", the TiN etch rate is about 62 Å/min. With 1.5% "compound A" in the formulation the TiN etch rate is nearly doubled. To further enhance TiN/Cu etch rate selectivity, another novel TiN etch enhancement component, "compound B", was added to a formulation containing 1% of "compound A". The resulting TiN etch rate is increased with "compound B" concentration at 45 ºC as shown in Fig. 3. Fig. 2 and 3 show a low Cu etch rate overall (<2Å/min), and that "compound A" and "compound B" have no impact on Cu etch rate at 45 ºC.

Fig. 4 shows the TiN and Cu etch rates versus pH at 45 ºC for formulations containing 1% "compound A". The TiN etch rate increases with increasing pH because the etch rate is directly related to HO_2^- species concentration [1]. As the pH increases, the concentration of HO_2^- also increases, resulting in a higher TiN etch rate [2]. Fig. 4 also shows that the TiN etch rate can be tuned by simply adjusting the pH. To obtain a constant TiN etch rate while maintaining H_2O_2 concentration unchanged, it is important to keep pH unchanged. The Cu etch rate remains very low (<2 Å/min) throughout the pH range studied due to the presence of the copper corrosion inhibitor.

Metal etch rates of various formulations are shown in Table I. By increasing process temperature from 30 to 40 ºC, the TiN etch rate of HCX-T002C is increased from 30 Å/min to 65 Å/min. HCX35a with 1.5% "compound A" shows a higher TiN etch rate (250 Å/min) vs. the TiN etch rate of HCX35 with 1% "compound A" (200 Å/min), however, the Cu etch rate is excessive for HCX35a, and the formulation is not compatible with Cu. HCX35-1 with 1% "compound A" and 5% "compound B" shows a 233 Å/min TiN etch rate and a low Cu etch rate (<2 Å/min).

Fig. 5 illustrates (via SEM) two progressions of TiN etching with process time at 55 ºC. In the first (Fig. 5 a-c), HCX35 creates the TiN pullback after 60 seconds and complete TiN removal after 120 seconds. In the second (Fig. 5 d-f), HCX35-1 creates a significant TiN pullback after 30 seconds, and complete TiN removal after 90 seconds. After 60 seconds process time the TiN mask is almost completely removed by HCX35-1 compared with HCX35 which shows only the TiN pullback morphology in the same amount of time.

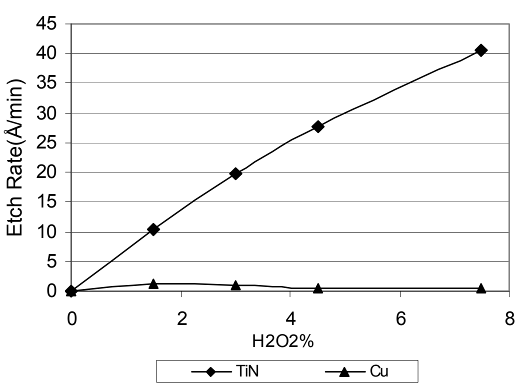


Figure 1. TiN and Cu etch rate vs. H_2O_2 % at 30 ºC (pH: 9.2)

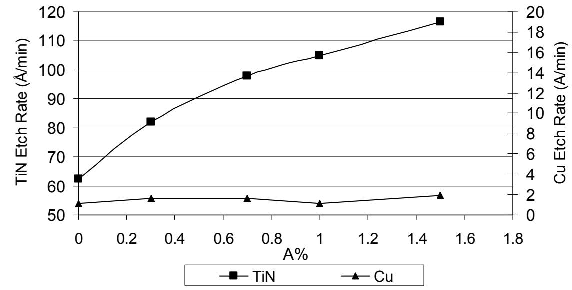


Figure 2. TiN and Cu etch rate vs. comp. A% at 45 ºC (H_2O_2 fixed, pH: 8.8)

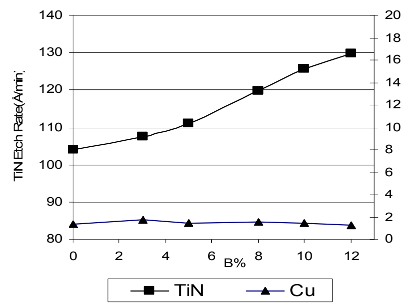


Figure 3. TiN and Cu etch rate vs. comp. B% at 45 ºC (H_2O_2 fixed, pH: 8.8)

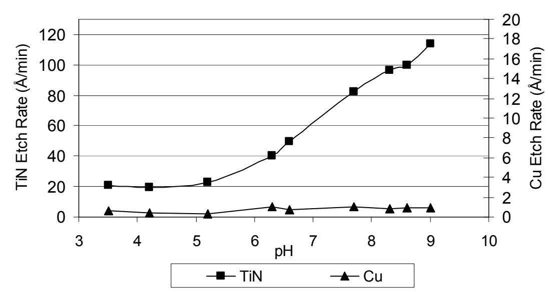


Figure 4. TiN and Cu etch rate vs. pH at 45 ºC

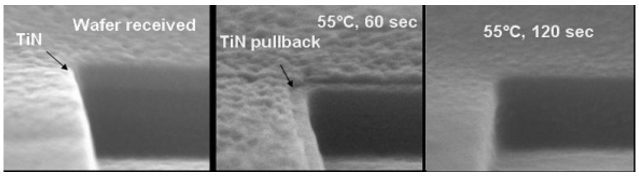
The effect of various formulations on the dielectric material etch rates are shown in Table II, which highlights the low impact of formulations on low-k, SiON and TEOS dielectrics.

Fig. 6 shows the etching residues after dry etching using TiN as an etching mask. Fig. 7 shows the complete removal of these etching residues after treatment with HCX-T002C at 45ºC for 2 minutes, and also shows the TiN pulled-back morphology.

The SEM in Fig. 8 and 9 show the effect of the formulas on copper oxidation. Fig. 8(a) shows that CuO_x [3] was re-grown after a 5 minute DIW rinse and dry. Fig. 8(b) and Fig. 9(a) and (b) show that there are no CuO_x formations after Cu was treated with HCX-T002C, HCX35 and HCX35-1 respectively, demonstrating that all three formulas have the ability to prevent CuO_x growth.

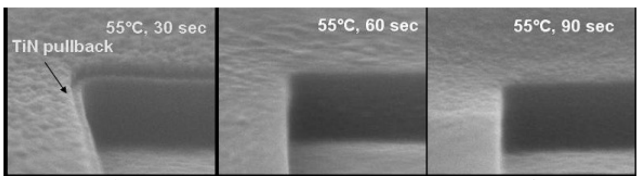
TABLE I. FORMULATION AND ETCH RATE ON METALS

Formulation	Chemical		Metal Etch Rate			
	Comp A%	*Comp B%*	*Temp (°C)*	*TiN (Å/min)*	*Cu (Å/min)*	*Co (Å/min)*
HCX-T002C	0	0	30	30.5	0.43	0.42
			40	65.23	0.46	2.01
HCX35	1	0	55	200.0	1.14	N/A
HCX35a	1.5	0	55	250.0	3.0	N/A
HCX35-1	1	5	55	233.0	1.8	N/A



(a) (b) (c)

HCX35



(d) (e) (f)

HCX35-1

Figure 5. TiN Etch SEM for HCX35 and HCX35-1

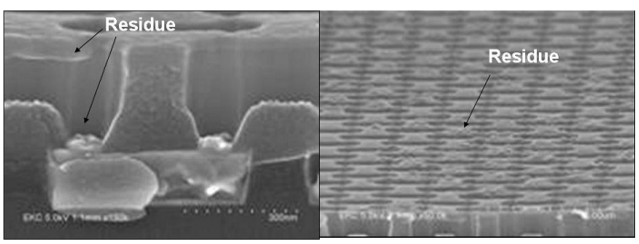


Figure 6. Wafer SEM as received

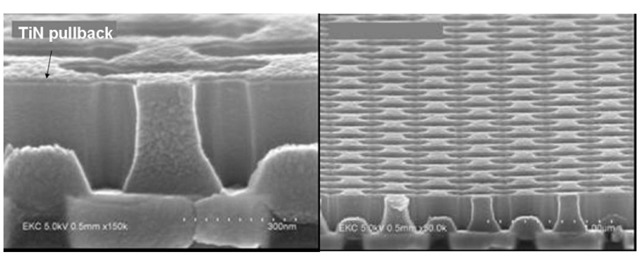
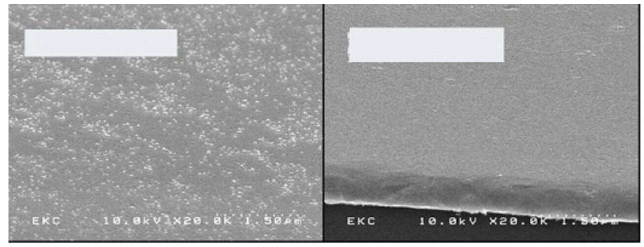


Figure 7. SEM after cleaning at 45 ºC, 120 sec (removed residues, formed a TiN pullback)

IV. SUMMARY

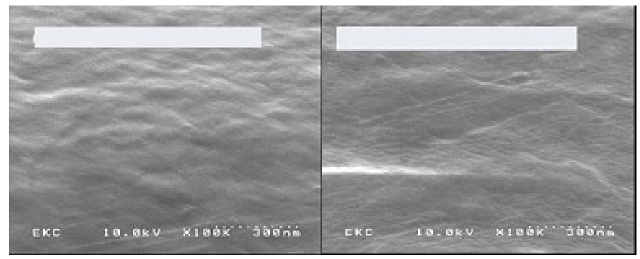
The formula, HCX-T002C, with a TiN/Cu etch rate selectivity of more than 60 has been developed. The formula is compatible with Cu, Co, low-k, TEOS and SiON dielectric materials and is able to remove all etching residues. This formula prevents Cu oxidation during and after cleaning, thereby relaxing queue-time restrictions between cleaning and subsequent process steps.

HCX-T002C is ideal for applications that benefit from TiN mask pullback morphology. HCX35 and HCX35-1 formulations with TiN/Cu etch rate selectivity greater than 200 have been developed. These formulations are compatible with Cu, low-k, TEOS and SiON materials, and prevent Cu oxidation during and after cleaning. The etch residue cleaning performance of these formulations are currently under study.



(a) (b)

Figure 8. Two Cu coupons with CuOx removed: (a) 5 min DIW rinse only (b) Treated with HCX-T002C chemical at 50 °C for 2 min and then 5 min DIW rinse



(a) (b)

Figure 9. Two Cu coupons with CuOx removed: (a) Treated with HCX35 at 55 °C for 2 min, then 5 min DIW rinse (b) Treated with HCX35-1 at 55 °C for 2 min and then 5 min DIW rinse

TABLE II. ETCH RATE ON VARIOUS DIELECTRIC MATERIALS

Formulation	Temp (°C)	TEOS (Å/min)	ULK (Å/min)	SiON (Å/min)
HCX-T002C	30	0.75	0.455	0.035
	46	-1.05	0.6	0.435
HCX35	55	1.68	0.81	0.82
HCX35-1	55	0.87	0.92	0.76

REFERENCES

[1] S.Verhaverbeke, J.W.Parker, “AModel for the Etching of Ti and TiN in SC-1 Solutions”, Mat.Res.Soc.Symp.Proc. Vol.,477, pp.447-458, 1997.

[2] H.Cui, M. Claes and S. Suhard, “TiN Metal Hardmask Etch Residue Removal on Advanced Porous Low-k and Cu Device with Corner Rounding Scheme”, Ultra Clean Processing of Semiconductor Surfaces (UCPSS), 2010.

[3] M. Kodera, Y.Nishioka, S, Shima et al, “Localized Oxidation of the Cu Surface after Chemical Mechanical Planarization Processing”, Jpn. J. Appl.Phys.,Vol.,44(12),pp.8396-8400,20