Suppression of galvanic corrosion in advanced BEOL integration

EXECUTIVE OVERVIEW A single wafer closed chamber system has been developed to control oxygen levels during processing. This control has enabled the use of hydrofluoric acid for post etch cleans of advanced (32nm) BEOL processes. Without oxygen control, processing with hydrofluoric acid is not possible due to excessive corrosion of the exposed materials.

Low oxygen, dilute hydrofluoric (dHF) acid cleaning, permitted by the unique, closed chamber design of a new single wafer cleaning tool, is a critical enabler for advanced (32nm) BEOL processes. It reduces corrosion of the capping layer required to prevent copper electromigration. The use of dHF acid in copper back end of the line (BEOL) post etch cleans is well established [1-4]. However, its viability in advanced processes is called into question by the increased sensitivity of advanced integration schemes to the amount of copper loss that is inherent with current dHF processes.

The International Technology Roadmap for Semiconductors (ITRS) also identifies reliability issues, associated with copper electromigration, as a significant issue in advanced BEOL integration [5]. TaN currently prevents electromigration along the damascence via and trench sidewalls, but with smaller device geometries, electromigration along the top surface of the copper line must also be prevented. Copper capping layers that can prevent electromigration on the top surface are under evaluation for 32nm processes. The most studied and likely candidate is an electrolessly deposited cobalt tungsten phosphide (CoWP) film often referred to as a self-aligned barrier (SAB) [6]. Although this SAB is effective at preventing electromigration, exposure of both copper and CoWP to dHF permits a galvanic corrosion mechanism that ultimately consumes the CoWP layer. Oxygen is required in both corrosion pathways [7] (**Fig. 1**). The closed chamber design of FSI's Orion single wafer cleaning system makes it possible to control oxygen levels in the process environment, reducing corrosion and enabling the use of CoWP capping layers.

It is also worthwhile to mention two other requirements identified in the ITRS Interconnect chapter related to post etch cleans. These requirements are for <2.5% effect on the low-*k* dielectric constant and <1.5% effect on critical dimensions [8]. This also becomes more challenging with porous low-*k* dielectrics. dHF gives the flexibility to control temperature and concentration to meet the specifications in the ITRS. Depending on the integration scheme (e.g., metal vs. non-metal hard mask), dHF concentrations can be varied easily from 100:1 to >1000:1 to accommodate the integration scheme. The work presented here utilized dHF concentrations in the range from 100:1 to 500:1.

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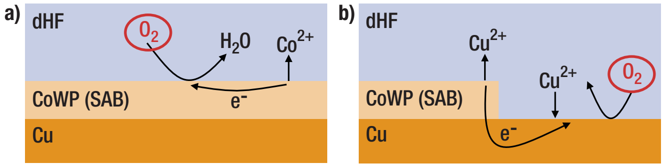
CoWP corrosion without exposed copper is presented to illustrate that, even without galvanic coupling, corrosion does occur. Oxygen in solution will oxidize the cobalt, resulting in a species that can further react in acidic media to liberate cobalt from the surface. Copper will corrode by the same reaction path as shown in Fig. 1a [9]. This fact helps us understand the results presented in this article. The experiment uses blanket copper wafers to determine the compatibility of a dHF post etch clean for advanced BEOL integration schemes.



Overall reaction

$Co + O_2 + 4H^+ + 2e^- \rightarrow Co^{2+} + 2H_2O$

$Co + 2H^+ \rightarrow Co^{2+} + H_2$

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$Co + O_2 + 4H^+ + 2e^- \rightarrow Co^{2+} + 2H_2O$

$Cu^{2+} + Co \rightarrow Cu + Co^{2+}$

Figure 1. Oxygen containing dHF corrosion of a) CoWP (similar corrosion reaction for copper), and b) CoWP in the presence of copper accelerated due to galvanic corrosion mechanism.

Corrosion is more evident when both copper and CoWP are exposed in dHF. A galvanic cell is established, accelerating corrosion of the less noble material (CoWP SAB layer) [7]. The loss can be significant enough to completely dissolve the CoWP layer. This unacceptable situation requires modification of the currently implemented dHF processes in single wafer open chamber systems.

Overcoming incompatibility in previously implemented dHF BEOL post etch cleans requires oxygen elimination [7,9]. Removing oxygen minimizes copper/CoWP oxidation, creating a stable surface in the presence of dHF. When copper and CoWP are exposed, the anodic half cell reaction oxidizing the CoWP is eliminated, stopping the galvanic corrosion sequence. This approach is taken for dHF post etch cleans implementation with advanced BEOL integration. Oxygen has been removed from the dHF process without corrosion inhibitors or oxygen scavengers. A single wafer closed chamber system has been developed and incorporated into the single wafer cleaning system to enable dHF use for advanced BEOL integration post etch cleans [10].

Removing oxygen from the cleaning fluids is also essential for dHF compatibility with copper and SAB. The processing chamber atmosphere also must be effectively controlled to a low level of oxygen. Without controlled oxygen levels in the fluids and chamber atmosphere, a dHF-only system implementation will be unsuccessful.

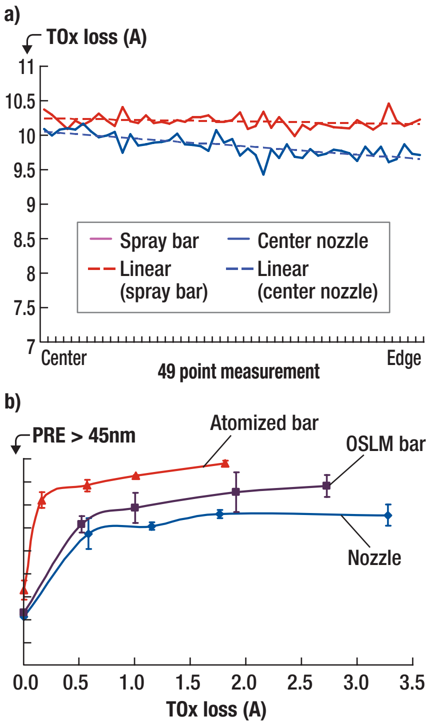


Figure 2. a) dHF etch uniformity and b) SC1 PRE of three dispense modes in the closed chamber system. Dispensing via the spray improves both uniformity and PRE.

The single wafer closed chamber system can dispense fluids via two main modes: a nozzle fixed above the center of the substrate or a spray bar dispensing fluids across the radius of the substrate with or without atomization. Atomized fluids in a single wafer closed chamber with a controlled atmosphere provide process benefits (**Fig. 2**) typical of an atomized fluid stream (increased PRE, uniform chemical distribution, and increased mass transport) in the closed chamber controlled environment.

An improved etch uniformity is possible with the spray bar dispense when compared to a center fixed nozzle dispense. PRE is also increased with a spray bar dispense (Fig. 2b). High PRE is achieved with the atomized spray bar dispense and low TO$_x$ loss (< 0.2Å). Without atomization, higher material loss is required (>>1Å) to achieve similar PRE.

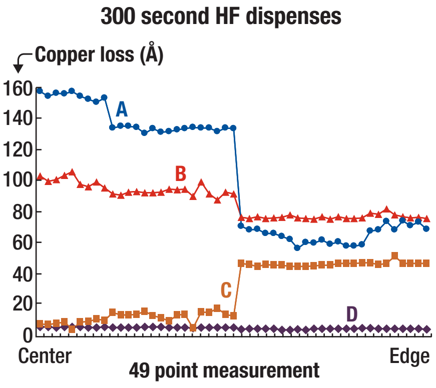
To evaluate the single wafer closed chamber's ability to control oxygen levels during dHF processing, blanket copper wafers were used as an evaluation metric. Blanket copper wafers were useful to gauge the success of the low oxygen processing, and provide information regarding the source of oxygen if copper loss was higher than desired. The dissolved oxygen level for optimum performance was targeted at <100ppb in the processing fluids.

A Signatone QuadPro four-point probe measurement was performed before and after processing to determine copper loss. The phrase copper loss is used loosely in these evaluations. The four-point probe measurement does not account for the native copper oxide that will always form whenever the copper surface is exposed to air (in the FOUP, during measurement, etc). The native copper oxide will be removed by the dHF regardless of the level of oxygen present during processing. Once the native copper oxide layer is removed during processing, the underlying non-oxidized copper corrosion will depend on the level of oxygen present during processing. Native copper oxide thickness that will form readily under ambient fab conditions is 10–15Å [11]. Therefore, "copper loss" in this range can be senn as caused by the native copper oxide.

The 49-point copper round maps measured on the four point probe show interesting details depending on the level of oxygen in the fluids or chamber atmosphere. There are three regions of importance when referring to 49-point round maps. The first region consists of nine data points including the wafer center and eight data point in a ring around the center. The next region of sixteen data points are midway between the center ring and the last region or outer ring, which is close to the wafer edge. This outer ring consists of the last twenty-four data points. Four processing conditions are shown in **Fig. 3** with varying levels of oxygen in the processing fluids and chamber environment illustrating the copper loss profile variations.

Conditions A and B have low, controlled oxygen levels in the chamber environment but high levels of oxygen in the dHF (Fig. 3). This results in a copper loss profile high in the wafer center. The lower copper loss at the edge of the wafer also indicates the fluid is losing oxygen as it flows across the wafer surface and is exposed to the controlled low oxygen levels in the chamber atmosphere.

A contrasting profile is observed by reversing the levels of oxygen in the fluid and chamber atmosphere. Low levels of oxygen in the dHF but ambient levels in the atmosphere creates a copper loss profile that is high near the wafer edge (condition C). Similar but opposite to conditions A and B, the fluid is absorbing oxygen as is travels across the wafer surface, resulting in more copper loss at the wafer edge. Both of these unacceptable conditions will result in corrosion of the copper and SAB layer.



	O$_2$ levels	
	HF	Chamber environment
A	~8ppm	Low
B	~4ppm	Low
C	<100ppb	High
D	<100ppb	Low

Figure 3. Control of oxygen levels both in the fluids and chamber environment is required for suppression of copper corrosion as shown by processing condition D.

Oxygen must be controlled in the processing fluid and chamber atmosphere to suppress copper corrosion. This is shown by condition D. Both the dHF and chamber atmosphere have controlled, low levels of oxygen, resulting in a flat copper loss profile with very low total copper loss. For this condition, the total copper loss was <10Å for a 300s dHF dispense, well within the expected thickness of a native copper oxide layer.

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Galvanic corrosion continued from page 13

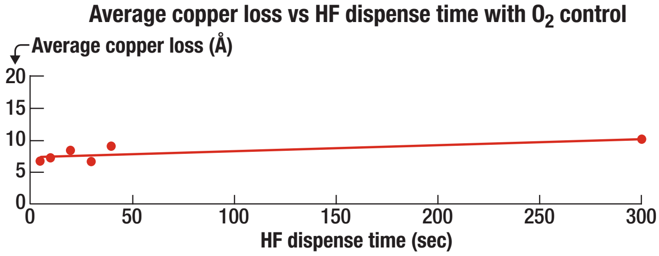

Figure 4. Similar amounts of copper were removed regardless of process time, indicating that the majority of the copper removed was the result of native copper oxide formation.

Further examining the copper loss attributed to the native copper oxide formation, copper loss as a function of HF exposure time was investigated. dHF dispenses of 5, 10, 20, 30, 40, and 300 seconds show similar average copper losses with proper oxygen control in the fluid and closed chamber atmosphere (**Fig. 4**). The majority of material loss is due to growth and dissolution of the native copper oxide by dHF. Attributing the shorter dHF dispense time copper losses to native copper oxide and comparing the copper loss to the 300sec. dHF dispense results in a copper etching rate of <0.4Å/min in the single wafer closed chamber system. Without correct oxygen control, the copper loss is >20Å/min, far above the thickness attributed to native copper oxide formation.

Conclusion

The data presented confirms the ability of the single wafer closed chamber system to reduce and effectively control oxygen levels. This was accomplished without the addition of corrosion inhibitors or oxygen scavengers. Applying this approach to the more sensitive system where copper and CoWP SAB are exposed and susceptible to galvanic corrosion has proven successful as well. As part of a 32nm BEOL development program, this system has been successful in eliminating CoWP corrosion across the entire wafer surface; corrosion that would otherwise be present without the complete control of oxygen in the processing fluids and chamber environment.

The specific integration scheme dictates the dHF conditions most appropriate for the materials involved. The single wafer closed chamber system allows for additives, such as organic acids, to the dHF if a metal hard mask integration scheme is used. The system design is not exclusive to oxygen-sensitive processing, as shown by the current integration into 45nm BEOL dHF processing. Lastly, the technique of oxygen control can be extended into the FEOL for dHF processing of high-*k* metal gates where galvanic corrosion issues have been identified in the presence of oxygen [12]. ■

References

1. L. Broussous, O. Hinsinger, S. Favier, P. Besson, in *Post-etch Cleaning Chemistries Evaluation for low- k Copper Integration*, Solid State Phenomenon: 2002; p 263.
2. K. Ueno, V. M. Donnelly, T. Kikkawa, "Cleaning of CHF3 Plasma-Etched SiO2/SiN/Cu Via Structures with Dilute Hydrofluoric Acid Solutions," *J. Electrochem. Soc.* **1997**, 144, (7), 2565.
3. L. Broussous, W. Puyrenier, D. Rebiscoul, V. Rouessac, A. Ayral, in *Porous low-k wet etch in HF-based solutions: focus on cleaning process window, "Pore-sealing" and "K Recovery"*, Solid State Phenomenon: 2009; pp 295-302.
4. Y. Travaly, et al., In *Key factors to sustain the extension of a MHM-based integration scheme to medium and high porosity PECVD low-k materials*, IITC 2008; p 52.
5. ITRS, Interconnect. **2007**, Technology Requirements.
6. S. Chhun, L.G. Gosset, W. Besling, T. Vanypre, P. Brun, E. Oilier, et al., in *Integration of multi-level self-aligned CoWP barrier compatible with high performance BEOL*, IITC, 2006.
7. S. Bilouk, C. Pernel, L. Broussous, V. Ivanova, R.P. Nogueira, in *Electrochemical behavior of cobalt in post-via clean solutions*, Solid State Phenomena: 2009; pp 343-346.
8. ITRS, Interconnect. **2007**, Table INTC4a.
9. D. Levy, F. Tardif, F. Maunier, C. Pizzetti, K.K. Christenson, in *The control of dissolved gasses in aqueous-based semiconductor processing*, ECS Proc., 2000; p 121.
10. J. M. Lauerhaas, in *Reduced Oxygen Cleaning Process for Advanced Cu/low-k Integration*, SEMATEC Surface Preparation and Cleaning Conference, March 23 - 25, 2009.
11. T.-K. Kang, W.-Y. Chou, "Avoiding Cu Hillocks during the Plasma Process," *Jour. of the Electrochemical Society* **2004,** 151, (6), G391-G395.
12. S. Garaud, R. Vos, D. Shamiryan, V. Paraschiv, P. Mertens, J. Fransaer, S. DeGent, in *Galvanic Corrosion of Stacked Metal Gate Electrodes During Cleaning in HF solutions*, Solid State Phenomena: 2006; pp 87-90.

Acknowledgment

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