Development and Application of BEOL Polymer Residue Removal Technology

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Abstract

Among the technical nodes at 90nm and below, copper/low-k interconnect possesses the characteristics of falling resistive-capacitive (RC) delay, low interconnect resistance and high reliability, which is commonly used to replace traditional aluminum/silicon dioxide in interconnection technology. Since copper cannot react with the etch gas to form volatile by-products, copper metallization is unsuitable for the process of dry etching, and dual damascene integration scheme is used for BEOL interconnection. The wet chemistry post-etch clean is an essential step in dual damascene technology, and it is primarily used to eradicate the post etch residue. Throughout the cleaning process, low-k, Cu, Ta/TaN and other films in damascene will be exposed. Consequently, the cleaning solution must do less damage to numerous materials. In this work, two types of semi-aqueous wet clean chemicals (ST250 from ATMI and ICS8000 from Anji) are tested in FBĎ 300mm single clean tool. In the past, many factories struggled with the ball-type defects when using ST250 as post etch polymer remover. We keep addressing the ball-type defects by proposing one possible failure mechanism and presenting several solutions. The photo-assistant copper corrosion and potential chemical residue problem are also discussed.

1. Introduction

Wet chemistry post-etch clean is vital in BEOL process. At almost every few steps during the procedure, cleaning is involved. The quality of silicon wafer cleaning directly impacts the device's yield and reliability. According to C.F. Tsang et al, there are three main wet clean processes which involve the dual damascene structure formation. These steps are post-via etch, post-trench etch, and post Cu cap etch respectively [1]. By undergoing dry etch, the by-products such as CF , CuF , CuO, Cu O, polymeric residues and re-sputtered Cu are formed [2] [3]. Generally, the wafer's contamination from by-products is usually inevitable.

The single-wafer spin cleaning tool (Ultra C II) used in this article is made by FBĎ Research, Inc. This product has 8 chambers and each chamber is configured with four chemicals - Main chemical (ST250 or ICS8000), DHF, dual fluid spray and CO_2 gasified DI water. Two kinds of post-etch clean chemicals (ST250 and ICS8000) are tested and discussed in this article. Both ST250 and ICS8000 are fluorine-based semi-aqueous strippers and designed for Cu damascene cleaning. However, as shown in Table 1, ICS8000 features lower viscosity compared with ST250 both at room temperature and 40℃ which is the typical process temperature. It is expected that ICS8000 can be rinsed off by ultrapure water more efficiently compared with the viscous ST250, which may contribute to shorter rinse time and better particle performance.

Table 1. Viscosity comparison between ST250 and ICS8000

	ST250	**ICS8000**
Viscosity at 25℃ (mPa·s)	33.14	8.75
Viscosity at 40℃ (mPa·s)	17.25	5.70

In a volume manufacturing environment, concerning cost of consumption (CoC), both ST250 and ICS8000 need to be reclaimed every time and reused within up to 72hours of their lifetime. To control lifetime of both chemicals, two standards are proposed for the machine itself. The first is to strictly control the water concentration in the chemicals. The second is in reference to a high reclaim rate of the chemicals. If the water content is too high, fluorides dissociation will be enhanced, leading to a sharp increase in the etching rate of copper metal, which will cause the excessive loss of copper. If there is an excessive loss of water, reactive species will be reduced, which will have a direct negative impact on the cleaning effects and make the residue removal incomplete. Nevertheless, the etching rate of ST250 and ICS8000 does not change a lot within 72hours of the bath lifetime, because the tool could be used in three different DI water dosing methods (1.by reclaimed chemical volume; 2. by lifetime; 3.by process time of chemical) to control the concentration of the chemicals cooperatively or separately. Moreover, the tool has a 99.17% reclaim rate, and 30L of liquid is enough to meet the 3-day demand.

Within the experiment, several important parameters are firstly designed to test, such as particle addition and removal, etch rate checks and the control of the effects of water concentration. Secondly, after running the KLA inline defect check (pattern wafer with single damascene structure), special particle maps in which particles are concentrated in center of wafer and looked like ball-shape under the SEM after ST250 cleaning were found. Through continual speculation and improvement, the ball defect issue was successfully resolved by using low-viscosity ICS8000 or by process tuning in the FBO single-wafer tool. Meanwhile, from experimental results, some BEOL cleaning common issues, including photo-assistant copper corrosion failures and residue remaining problems can be avoided effectively in the tool.

2. Experimental and Discussion

Particle addition is defined as the delta of particle count before and after wet clean. Particle addition is crucial in metal interconnection, as particles may lead to poor electrical property, which therefore affects the yield and performance of devices. ST250 and ICS8000 are individually tested using 16 pieces of 300mm wafers coated with a thin layer of PECVD oxide in two different chambers. The temperatures of chemicals are 40 . Fig. 1 shows the particle addition at 80nm size for both ST250 and ICS8000 with 16 consecutive runs. From the results, particle (≤80nm) adding for both chemicals is all well controlled and less than 10ea after cleaning.

Fig. 1. The particle adding situation on PECVD oxide blanket wafers after using ICS8000 and ST250 treatment.

Dual fluid spray is a technology that uses high pressure gas to drive the liquids, forming a mist and high-speed injection to the wafer surface, which combines physical force with chemical reaction to assist nano-size particle removal and post etch polymer removal. Fig. 2 (a) and (b) compares on the same batch of single-damascene structure wafer, whether or not to use the dual fluid spray, and the results show that the joining of dual fluid spray has made obvious improvements in removing the residues and particles.

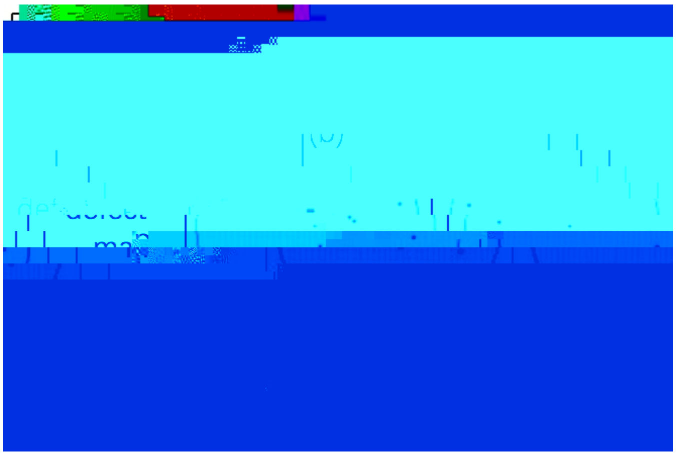
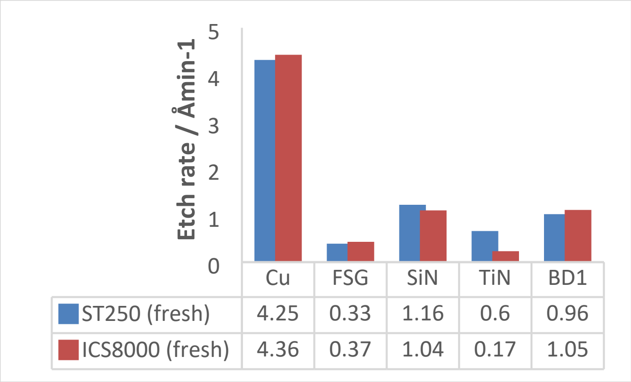


Fig. 2. (a) Particle count without using dual fluid spray. (b) Particle count after adding 15s dual fluid spray in the same process and same batch of single-damascene structure wafer.

The etch rate is another key parameter for the removal of post-etch residue, and excessive etching will induce film lose, can cause electrical property problems. In this experiment, etch rates of films at the initial stage of processing and after 72 hours of ST250 and ICS8000 processing are collected respectively. The temperature is the same as particle check. Fig.3 illustrates that both chemistries are compatible with typical BEOL dielectric and metal films, and the etch rate of Cu and low-k materials is less than 5Å /min.



	Cu	FSG	SiN	TiN	BD1
🟦 ST250 (fresh)	4.25	0.33	1.16	0.6	0.96
🟥 ICS8000 (fresh)	4.36	0.37	1.04	0.17	1.05

Fig. 3. Comparison of the etch rate for different films at 40℃

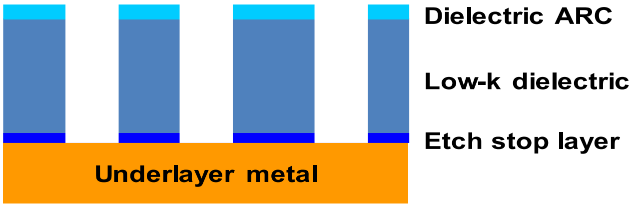


Fig. 4. Schematic of the single damascene structure in this test.

The single damascene structure wafers were prepared by the conventional DUV lithography and dry etch sequence, as shown in Fig. 4. After the etch stop layer is etched, the underlayer metal film is exposed. Before the deposition of next-level metal layer, the wafers were cleaned in FBǰD single-wafer tool by using ST250 and ICS8000. Dark-field defect inspection tool was used to scan the defect after wet clean. As shown in Fig. 5, the ST250 has a ball defect issue. The typical defect map shows a ring shape with the inner radium of around 20-30mm. SEM images reveal that these defects are mainly ball-type defect. Through mechanism analysis to solve this issue, improvements to the methods were made. On the other hand, when tested with the low-viscosity ICS8000, this type ball defect can not be observed.

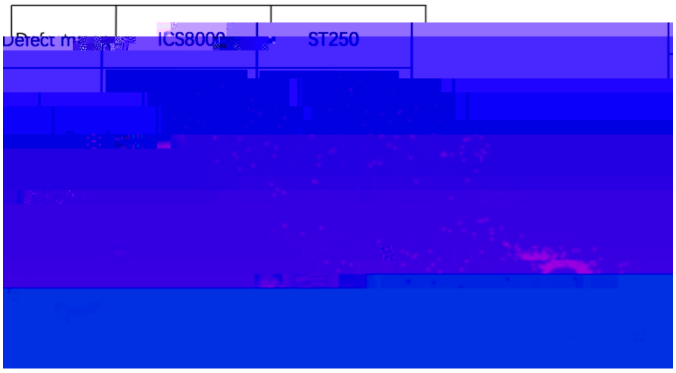


Fig. 5. Defect map for both chemicals and SEM top-view of defects at center of wafer after ST250 cleaning.

Hypothesis 1:

Hitoshi et al. found that in single-wafer wet cleaner, the local thickness of water layer is related to various parameters, such as wafer rotation speed and radical distance from wafer center [4]. As shown in Fig. 6(b), at the rotation rates of 200, 500 and 1400 rpm, the water layer thickness does not present steady curves as the radical distance changes. At the radial distance from wafer center of around 10mm, both liquid layer thickness and the radical velocity are much smaller than other zones (radical velocity profile is not shown). We suspected that the combination of thinner liquid layer thickness and slower radical velocity will result in poor chemical wetting at this local area, which consequently results in ball-type defect deposition. This phenomenon is more pronounced to high-viscosity chemical, such as ST250. The captured image in Fig. 6(a) also confirms this prediction. As shown in Table 1, viscosity of ICS8000 is much lower than ST250’s, which is the reason why ICS8000 does not suffer the ball-type defects (Fig. 5).

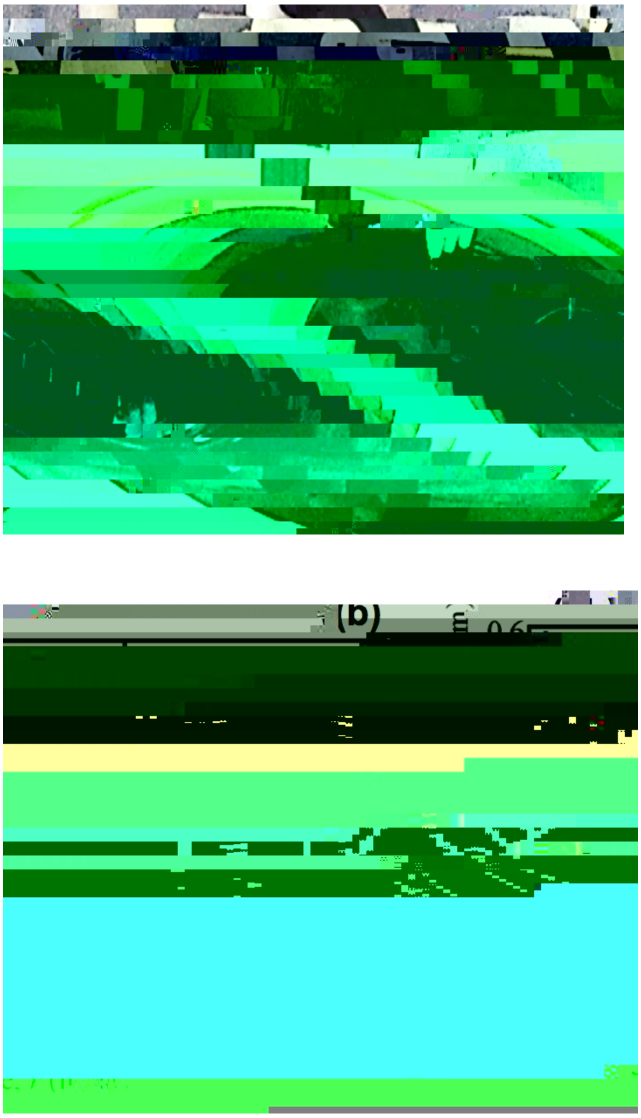


Fig. 6. (a) Captured image of ST250 layer thickness at a rotation rates of 400 rpm. (b) Water layer thickness profiles at the rotation rates of 200, 500 and 1400 rpm respectively [4].

Solution 1:

Using CO_2 gasified DI water to pre-rinse and pre-wetting the wafers, improve the wettability for ST250 and effective removal of electrostatic charge before the main chemical process. It can be seen in Fig. 7, the ball defect issue will no longer exist on these wafers which has pre-treat by the functional water.

Basing on the proposed failure mechanism and our experiment results, the ball-type defect can be prevented by using low-viscosity ICS8000 or by process tuning in the FBǰO single-wafer tool which both contributes to improve wettability of the chemicals.

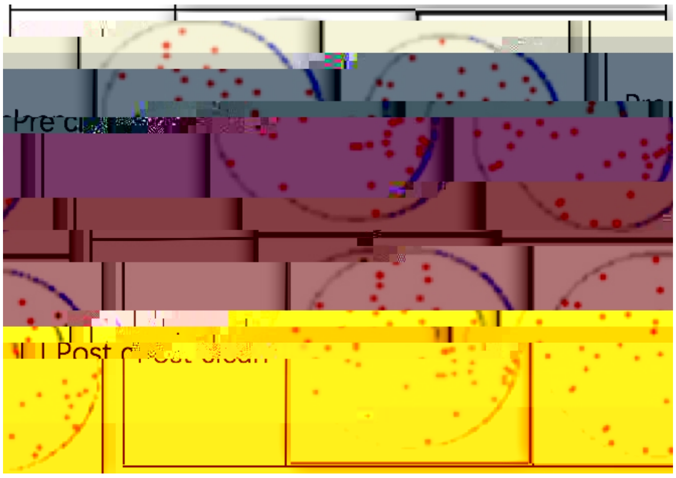


Fig. 7. Defect maps of ST250-cleaned wafers after adding CO_2 gasified DI water pre-rinse.

Hypothesis 2:

Dry etching is based on the charge accumulation effects caused by ion bombardment. In the etch process, when the plasma functions on the surface of the wafer, electrostatic fields will be easily produced simultaneously. In view of the accumulation of charge, there is a kind of polymer formed with a difficult removal property. For this reason, if static charge cannot be removed before the post-etch cleaning, it will result in a high possibility of secondary particle contamination.

Solution 2:

Conductive pins function to remove electrostatic charge within a short period of time. Two conductive pins are installed in each chamber to remove the electrostatic charge and effectively prevent the ball defect.

The mechanism of photo-assistant copper corrosion failure is simplified explanation in Fig 8. This kind of phenomena normally exists on certain specific integrated circuits. After wet cleaning process, the naked Cu is exposed in cleaning fluid. It will be migrated under high-energy light, which causes the copper interconnect to fail [5].

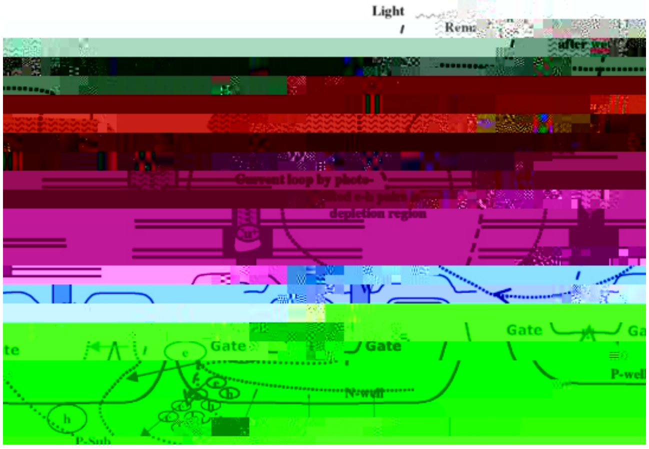


Fig. 8. Mechanism of photo-assistant copper corrosion failure [6].

The tools adopt chamber enclosed with a light-proof cover, which prevent the outside light from entering the chamber. Low-energy yellow light lamps are used in the chamber and will not be turned on during the cleaning process. This operation can effectively prevent the failure of photo-assistant copper corrosion.

The water content in ST250 and ICS8000 has a huge effect on the etch rate and cleaning efficiency. It will decline with chemical bath lifetime due to water evaporation at elevated temperature, and by not adding a certain amount of water, there will be performance variance with bath lifetime and bath lifetime is generally very short to ensure clean performance in the expense of chemical consumption. Hence, DI water dosing functions are added in the chemical delivery system (CDS). In the figure below, it adopts the mode 3, by process time of chemical, is adopted. That means when the chemicals process time that reaches the setting value, a set amount of water will be added into the CDS each time. NIR spectroscopy metrology (Horiba CS-100 series) is used to real-time monitor H_2O concentration in the chemistries. Fig. 9 shows usually within the three days' continuous process, the water content is tightly controlled between 38% to 40%, the variation of water content is tightly controlled within +/-3% , which reaches the needs of the process.

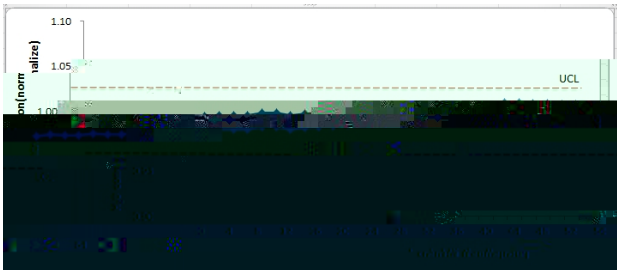


Fig. 9. Diagram showing the change in water content by continuous process within 3 days.

X-ray photoelectron spectroscopy (XPS) is a powerful tool to characterize chemical composition of wafer surface qualitatively and quantitative. In this study, Cu blanket wafers before and after ST250 or ICS8000 clean were inspected with the AXIS-ULTRA DLD XPS spectrometer. Fig. 10(a) shows the Cu $2p_{3/2}$ spectra for the Cu surfaces before clean and after cleaned with ST250 and ICS8000. The peaks located at around 932.5 eV can be assigned to Cu and/or Cu_2O. In addition, the high energy shoulders can be seen at the leftside of the main peaks, which can be assigned to a small amount of CuO on the Cu surfaces with binding energy at around 933.6 eV. Compared with the Cu surface before clean, both ST250 and ICS8000 clean suppress the intensity of the high energy shoulders because part of the surface CuO was removed by ST250 and ICS8000 clean. Also, it is noted that this effect is more pronounced for ICS8000. Fig. 10(b) exhibits the N 1s spectra for the Cu surfaces before and after clean with ST250 and ICS8000. The peak located at around 400.5 eV is assumed to be C-N groups. It is obviously observed that more contaminant containing C-N groups remained on Cu surface after ST250 clean. It is well-known that ST250 is very viscous even at 40℃ as shown in Table 1. After chemical process step, DI water rinse is conducted to rinse off chemical from wafer surface. In this test, DI water rinse at room temperature for 40s is adopted for both ST250 and ICS8000. With this rinse condition, the viscous ST250 was not completed rinsed off from the Cu surface. One of the components of ST250 which contains C-N groups remained on Cu surface and detected by XPS N 1s spectrum. On the other hand, with the same rinse condition (e.g., 40s at room temperature), ICS8000 can be rinsed off from the Cu wafer surface efficiently and not any chemical residue was detected by the sensitive XPS analysis as shown in Fig. 10(b).

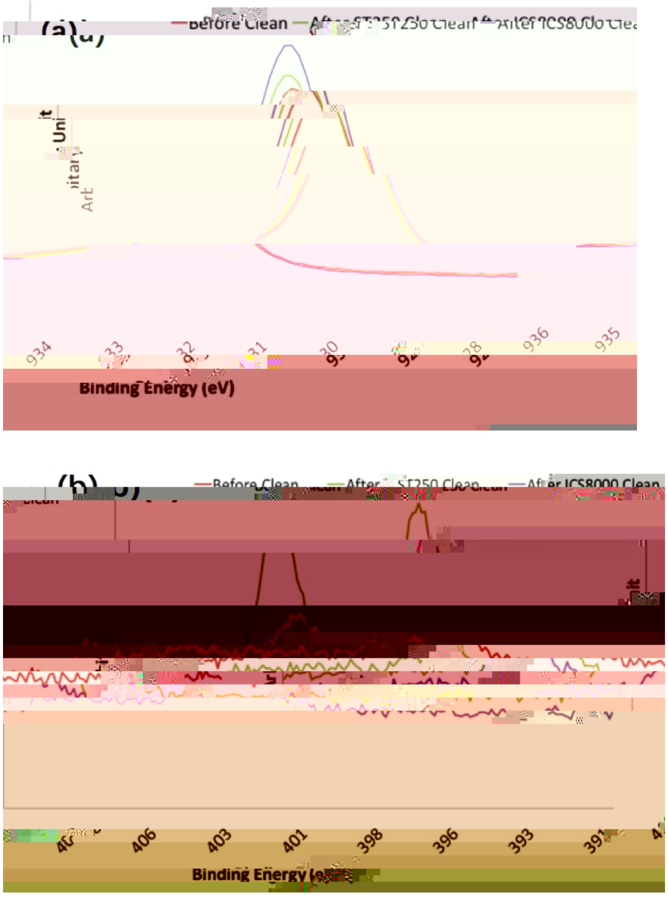


Fig. 10. XPS spectra in the (a) Cu $2p_{3/2}$ and (b) N 1s regions for the Cu surface before clean, after ST250 clean, and after ICS8000 clean.

Conclusion

Throughout the course of removing Cu post etch residue, FB[illegible] single wafer cleaning machine Ultra C II provides a good platform for ICS8000 and ST250. For example, using adopt chamber enclosed with a light-proof cover to avoid photo-assistant copper corrosion failure, using dual fluid spray to improve particle remove efficiency, adding conductive pins to prevent the absorption of ball defect. Meanwhile, CDS with manifold dosing allows the concentration of chemicals to remain stable in the process and extended bath lifetime is obtained.

Both ST250 and ICS8000 show good chemical compatibility with typical BEOL dielectric and metal films, however, ICS8000 features low-viscosity that will prevent ball-type particle deposition and provide more clean Cu surface.

Acknowledgement

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