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Research Article

Substrate Effect on Plasma Clean Efficiency in Plasma Enhanced Chemical Vapor Deposition System

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The plasma clean in a plasma-enhanced chemical vapor deposition (PECVD) system plays an important role to ensure the same chamber condition after numerous film depositions. The periodic and applicable plasma clean in deposition chamber also increases wafer yield due to less defect produced during the deposition process. In this study, the plasma clean rate (PCR) of silicon oxide is investigated after the silicon nitride deposited on Cu and silicon oxide substrates by remote plasma system (RPS), respectively. The experimental results show that the PCR drastically decreases with Cu substrate compared to that with silicon oxide substrate after numerous silicon nitride depositions. To understand the substrate effect on PCR, the surface element analysis and bonding configuration are executed by X-ray photoelectron spectroscopy (XPS). The high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) is used to analyze microelement of metal ions on the surface of shower head in the PECVD chamber. According to Cu substrate, the results show that micro Cu ion and the CuO_x bonding can be detected on the surface of shower head. The Cu ion contamination might grab the fluorine radicals produced by NF_3 ddissociation in the RPS and that induces the drastic decrease on PCR.

1. INTRODUCTION

In semiconductor manufacturing, the nitrogen trifluoride (NF_3) is widely used for plasma-enhanced chemical vapor deposition (PECVD) chamber cleaning due to its almost 100% dissociation in a discharge [1]. In PECVD system, the chemical precursors are excited by plasma to produce dielectric or metallic thin films on silicon wafers. However, deposition occurs not only on the wafer, but also on the exposed internal surfaces of the deposition chamber. This residue needs to be removed in order to minimize potential yield loss due to particle contamination and to maintain process integrity. Many researchers have studied the benefit of using NF_3 as the reactor clean gas instead of perfluorocompounds (PFCs) [2–5] and the optimizing utilization efficiencies of NF_3 in a remote plasma system [1, 6–8]. But few reports are demonstrated on the substrate effect of the plasma clean efficiency, especially on the long term performance of the reacted chamber condition in semiconductor manufacturing.

In advanced ultra large scale integrated circuits (ULSI), the dual damascene structure has been implemented in back-end of line (BEOL) development. A typical schematic of dual damascene procedure is illustrated in Figure 1. The silicon nitride is generally used as an etching stop layer and a dielectric barrier in the dual damascene scheme. That might contact with two kinds of substrates such as dielectric insulator and Cu interconnect. In this article, the PCR efficiency in PECVD reactor has been studied on Cu and dielectric insulator substrates, respectively. The mechanisms for PCR deviation between the two substrates are proposed and discussed.

2. EXPERIMENT

All the dielectric thin films are prepared by a PRODUCER SE 300mm twin PECVD deposition system with a remote plasma system (RPS). Figure 2 shows a schematic of the remote plasma system and the reacted chamber used for the experiments. The shower head and chamber interior exposed to the plasma are constructed of aluminum alloy materials. To mimic the role of silicon nitride in the dual damascene structure, the silicon nitride is deposited on Cu and silicon

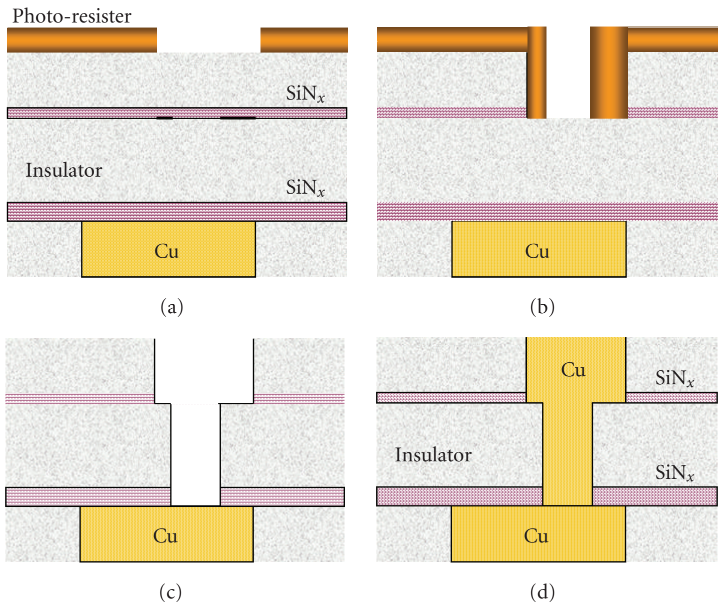


FIGURE 1: Schematic of typical dual damascene structure fabrication procedure: (a) stacked films with photo resister on top; (b) trench etching; (c) via etching; (d) Cu filling and polish process.

oxide substrates. The reaction precursors of silicon nitride and silicon oxideare $SiH_4 + NH_3 + N_2$ and $SiH_4 + O_2$ mixture gases, respectively, and those are injected into the reactor through the shower head. The chamber pressure, RF power, and deposition temperature are maintained at 4 torr, 600 W, and 400°C, respectively, throughout the deposition process. The Cu metal deposited on a silicon substrate is prepared by electro-Cu-plating (ECP) method. For better adhesion between Cu and silicon substrate, a silicon oxide is deposited as a buffer layer on the silicon wafer. It is well known that CuO_x is easily formed on the fresh Cu surface and that would induce the drift of electrical properties. Therefore, in order to remove the CuO_x, in situ NH_3 plasma treatment on Cu substrate has been introduced before silicon nitride deposition.

In PECVD system, the PCR is an important monitor index for the chamber condition and that is expressed as in the following formula:

$$\text{plasma clean rate (PCR)} = \frac{T_0 - T}{t} \text{ (nm/min)}, \quad (1)$$

where the T_0, T, and t are the primitive silicon oxide film thickness, silicon oxide thickness after NF_3 plasma etching, and etching process time, respectively. In this study, the PCR is monitored following the silicon nitride deposited on the different substrates. The film thickness of silicon oxide is measured by a reflectometer and/or ellipsometer with the KLA-Tencor FX-100. In total, 17 point measurements are taken on each wafer for averaging. To analyze the film composition and bonding configuration, the X-ray photoelectron spectroscopy (XPS) is examined on the substrate surface. The cross-section and surface morphology of Cu substrates with and without NH_3 treatment are performed by scanning electron microscope (SEM). To understand the effect of metal contamination on the shower head, the high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS, Thermo Finnigan Element) is used to analyze the metal microelement.

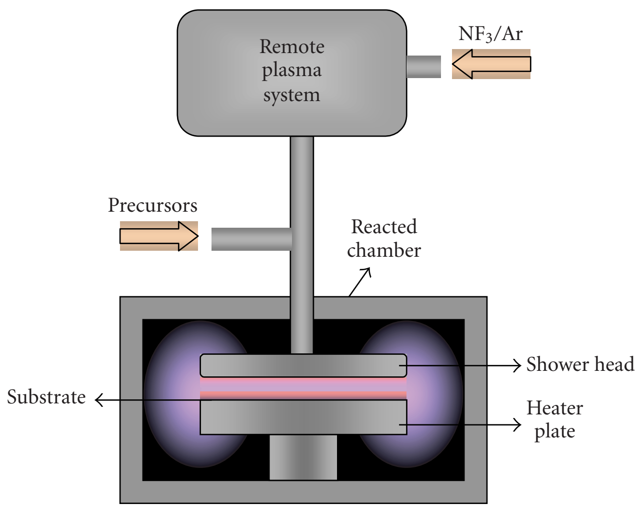


FIGURE 2: Schematic of the PECVD chamber with an RPS system in this experiment. The gases are injected into the reacted chamber through the shower head, and the substrate is placed in the center of a heater plate.

3. RESULTS AND DISCUSSION

In order to compare the substrate effect on the PCR, the Cu and silicon oxide substrates are simultaneously performed at chamber A and chamber B in PRODUCER SE 300 mm twin PECVD deposition system. Figure 3 shows the long-term PCR performances of the two chambers. It is apparent

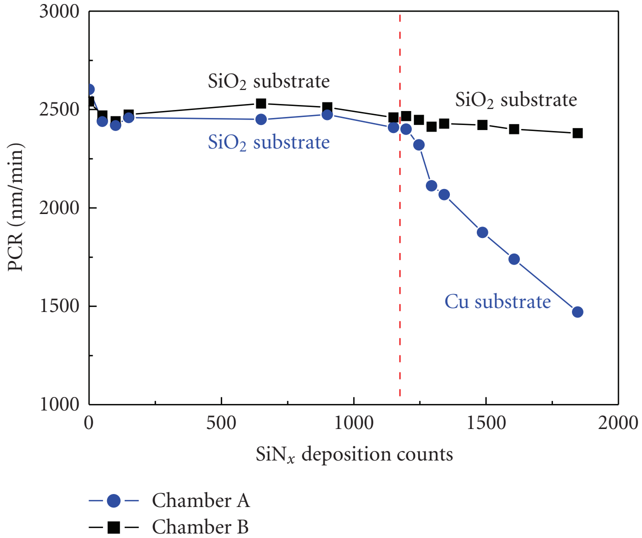


FIGURE 3: PCR as a function of SiN_x deposition counts on different substrates performed at PRODUCER SE 300 mm twin PECVD deposition system.

TABLE 1: Surface composition (atomic percentage) of fresh Cu substrate and Cu substrate with NH_3 plasma treatment.

	Cu%	O%	N%	C%	Si%	O/Cu ratio
Fresh Cu substrate	33.6	47.2	N/A	19.2	N/A	1.40
Cu substrate with NH_3 plasma treatment	20	55	N/A	19.7	5.3	2.75

that the PCRs are comparable for the two chambers at the silicon oxide substrate over 1000 piece deposition counts. That means that the chamber A and chamber B have similar chamber conditions, including shower head quality, plasma uniformity, and the interior surface of the chamber wall. Also, a drastic drop of PCR for chamber A has been observed after introducing Cu substrate. The PCR obviously deteriorates with the SiN_x deposition counts on Cu substrate compared with that on silicon oxide substrate. In Figure 3, after using Cu substrate, the slope of PCR for chamber A is about 27 times higher than that of chamber B (silicon oxide substrate). It suggests that the Cu substrate might play key role to degrade the PCR performance in a PECVD system.

To better understand the Cu substrate effect on the PCR decay, the surface morphology and composition of fresh and NH_3-treated Cu substrates are observed by SEM and XPS, respectively. Table 1 exhibits the surface composition of fresh Cu and NH_3 plasma-treated Cu substrate by XPS analysis. The results reveal that O/Cu ratio of fresh Cu substrate is 2 times less than that of NH_3-treated Cu substrate. The relative less Cu concentration of NH_3-treated Cu substrate implies that some Cu would disappear after NH_3 plasma treatment in the PECVD reactor. Also, it is noted that a few Si element is detected in the NH_3-treated Cu sample. Since the structure of stacking film is Si/SiO_2/ECP-Cu and the Cu thickness of ECP method is about 180 nm, the Si element beneath the thick

TABLE 2: Metal concentration of chamber shower head after numerous silicon nitride depositions on silicon oxide and Cu substrates.

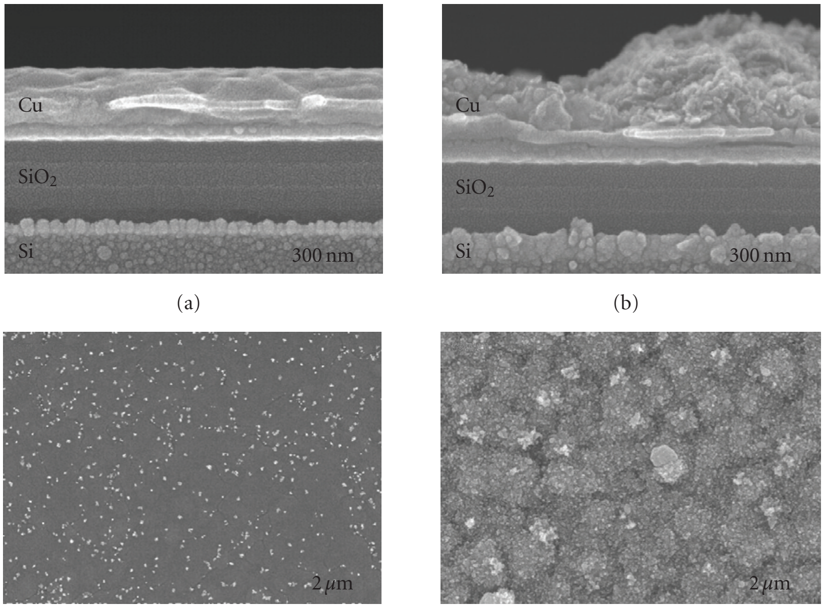
Condition	Element								
	Na	Al	Ca	Cr	Fe	Ni	Cu	Zn	K
Silicon oxide substrate	0.41	35	0.97	0.30	0.15	0.54	0.94	0.07	0.14
Cu substrate	0.3	39	0.95	0.26	0.27	0.33	6.30	0.12	0.15

Unit: ng/mL (ppb).

Cu film should not be detected in this NH_3 plasma treatment sample. The result suggests that the Si element might migrate from the silicon oxide underlying the Cu layer to the surface by NH_3 plasma bombardment which is agreed with the observation of cross-section image by SEM in Figure 4(b). Figure 4 shows the SEM cross-section and surface images of fresh Cu substrate and that with NH_3 plasma treatment. From Figures 4(a) and 4(b), it is obvious that the roughness of NH_3 plasma treatment sample is higher than that of fresh Cu sample. Also, Figure 4(b) presents a less continuous and looser structure of Cu film with NH_3 plasma treatment than that of the sample of as-deposited Cu film (Figure 4(b)). Figure 4(c) shows that the surface of the as-deposited Cu films is principally smooth and uniform compared to that of the NH_3-treated sample (Figure 4(d)). The results suggest that the Cu surface might be bombarded by NH_3 plasma and, as a sequence, the Cu scattered into the interior of the reactor by plasma discharge. That would attribute to Cu sprinkle in the deposition chamber, even more in the shower head. Sequentially, the Cu ions diffuse to the surface of shower head, and it supposedly traps the fluorine radicals dissociated from the NF_3 source by remote plasma system. As a result, the deteriorated PCR efficiency is attributed to the reduced fluorine radicals, those could react with silicon oxide to form the byproduct of silicon fluoride (SiF_x).

To clarify the afore-mentioned inference, the surface morphology and roughness of the shower head are examined by SEM and alpha-step. Figure 5 shows the SEM images and roughness of the shower head at different substrate conditions. The roughness ($R_{ave.}$) is the average of 17 point measurements for a shower head. From Figure 5(a), a level and smooth surface can be observed with the condition of silicon oxide substrate; on the other hand, a rugged surface that accompanies the condition of copper substrate is observed in Figure 5(b). It exhibits that ~40% reduction of surface roughness for silicon oxide substrate compared to that of Cu substrate. The results suggest that the shower head might be contaminated and damaged by Cu ions by using Cu substrate.

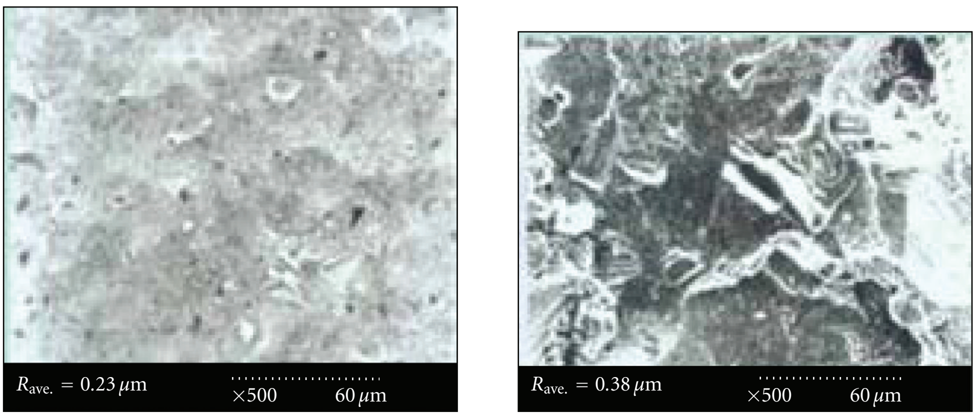
In order to verify the possible source that damaged the shower head, the metal concentration of shower head is studied by HR-ICP-MS analysis and the result is shown in Table 2. It is apparent that Al and Cu metal ions are the main metal elements in the two conditions. There is no doubt that the shower head consisted of Al alloy, therefore Al is the great quantity metal element in this analysis. No matter Cu or silicon oxide substrates, the relative Al concentrations are



(a) (b)

(c) (d)

FIGURE 4: SEM cross-section images of (a) fresh Cu substrate and (b) NH_3-treated Cu substrate. The corresponding surface morphologies of (c) fresh Cu substrate and (d) NH_3-treated Cu substrate.



(a) (b)

FIGURE 5: SEM surface images and surface roughness of shower head with over 1000 silicon nitride deposition counts on different substrates (a) silicon oxide substrate and (b) Cu substrate with NH_3 plasma treatment.

almost at the same value. For Cu concentration, almost one order of higher magnitude value can be detected in Cu substrate condition than that in silicon oxide substrate. It indicates that Cu source might come from the Cu substrate that is bombarded by NH_3 plasma treatment and then the Cu splashed to the reaction chamber. As a sequence, the splashed Cu in the plasma ambiance might impact or implant the shower head surface. Consequently, the Cu concentration in the shower head for Cu substrate sample is higher than that in silicon oxide substrate sample. The results coincided with Cu missing in Table 1 and Figure 4.

Based on the above results and inference, the possible mechanism and chemical reactions responsible for the PCR deterioration are expressed in the following reactions:

$$\begin{gathered} e^- + NF_3 \longrightarrow NF_x + F^-, \\ Cu + F^- \longrightarrow CuF_y, \end{gathered} \tag{2}$$

where the NF_3 is dissociated by electron impact from RPS; and the products of the dissociation steps are NF_x daughter species ($x = 1, 2$) and fluorine radical. In the shower head surface, the Cu ion coming from Cu substrate bombarded/excited by NH_3 plasma treatment would snatch the fluorine radical and produce the copper-fluoride compound on the surface of shower head. The consumption of fluorine source would deteriorate the PCR efficiency.

4. CONCLUSION

This article demonstrates the substrate effect, Cu and silicon oxide substrates on the long-term plasma clean rate performance. The Cu ion dominated the deterioration of PCR performance. As the evidence from the SEM morphologies and HR-ICP-MS results, the Cu ion source comes from the Cu substrate by NH_3 plasma bombardment and that sequentially damages the shower head. The possible mechanism and chemical reactions responsible for the PCR deterioration are proposed. Since silicon nitride as an etching stop layer in dual damascene structure has to be exposed to the NH_3 plasma and also the copper ion impact is inevitable, this work would be a good reference for optimizing the process parameters to minimize potential yield loss due to particle contamination reduction and process integrity maintenance.

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