Organosilane Downstream Plasma On Ultra Low-k Dielectrics: Comparing Repair With Post Etch Treatment

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Abstract

Plasma induced damage of ultra low-k (ULK) dielectrics is a common phenomenon in BEOL interconnects. The damage leads to an increase in k-value, which raises the RC delay, leading to increased power consumption and cross talk noise. Therefore, diverse repair and post etch treatments (PET) have been proposed to restore or reduce the ULK damage. However, current repair processes are usually based on non-plasma silylation, which suffers from limited chemistry diffusion into the ULK. Moreover, the conventional PET based on anisotropic plasma results in bottom vs. sidewall inhomogeneities of the structures (e.g. via and trench). To reduce these drawbacks, an organosilane downstream -plasma (DSP) was applied. This new application resulted in an increased resistance to ULK removal by fluorinated wet clean chemistries, preserving the ULK hydrophobicity, keeping its carbon content relatively high. The effective RC measured on 28 nm node patterned wafers treated with a DSP PET remains nevertheless comparable to the process of record (POR).

1. Introduction

Downscaling of integrated circuits’ (IC) increases the resistance (R) and capacitance (C) of interconnects. This leads to higher RC delay, power consumption and cross-talk noise. To counteract the capacitance increase, SiO\textsubscript{2} was substituted by low-k and ultra low-k (ULK) materials [1].

To lower the k-value of interconnect dielectrics, low polar bonds (C-C, C-H, CH\textsubscript{3}) and porosity were introduced [1]. However, porosity introduction made the low-k material more vulnerable to damage by the various process steps of the dual damascene integration. The dominant damage mechanism are damage during reactive ion etching (RIE) and plasma stripping, water uptake and undercut formation during wet cleaning, damage during pre-clean and deposition of the barrier-seed and damage related to slurry interactions during chemical mechanical polishing (CMP). Of all aforementioned issues, the plasma stripping is one of the most damaging processes [1]. This is because the stripping gases reduce the carbon content of the film, increasing the electric polarizability and consequently raising the k-value.

Trench-first-metal-hard-mask (TFMHM) integration approach was able to partially reduce this damage, since the plasma stripping is executed before the vias and trenches are completely etched [2]. In this case, the last step before wet cleaning is a post etch treatment (PET) executed in the Reactive Ion etching (RIE) chamber. Therefore, the PET will critically impact the low-k performance. Since after this process, the low-k material is exposed to aqueous wet cleaning chemistries, the low-k could lead to water uptake, consequently increasing the k-value.

There are several approaches for the dielectric recovery: Silylation, hydrocarbon plasma and thermal treatments assisted by UV light [1]

Liquid or vapor phase silylation (without plasma) has been extensively investigated to repair the low-k damage [3]. However, the repair molecules, in wet or non-plasma vapor phase, entail some steric hindrance effect that diminishes the reaction efficiency. Moreover, anisotropic plasma PET causes via-trench non-uniformities (of bottom vs. sidewall).

In this work, the vapor phase isotropic plasma approach will be studied. An organosilane, bis(dimethylamino)dimethylsilane (BDMADMS), downstream plasma process (DSP) was applied on ULK as repair and as PET (Figure 1) for carbon replenishment [4]. As a consequence, the isotropic plasma can improve the diffusion of the plasma fragments into the ULK pores and reduce the aforementioned trench bottom vs. side-wall inhomogeneities.

2. Experimental

BDMADMS with formula (Me\textsubscript{2}N)\textsubscript{2}Si(CH\textsubscript{3})\textsubscript{2} was selected for its abundant methyl groups with relative low vapor pressure (Vp= 10.1 Torr @ 25 °C) and thermal stability until at least 250 °C. As consequence, the mass flow can be precisely controlled. Furthermore, the presence of two amino groups improves the reactivity. Finally, a wide temperature window for experiments is allowed.

The DSP suppresses the energetic ion bombardment and enables a sidewall and bottom treatment of the via-trench. Two approaches with different integration processes were compared according to Figure 1. On the one hand, BDMADMS DSP was executed as repair approach. Abundance of silanol groups are required to provoke the silylation reaction [5]. Therefore, the silylation was assisted by executing the wet cleaning before the BDMADMS DSP. On the other hand, the BDMADMS DSP was executed as a new PET approach, replacing the original anisotropic PET.

All processes were executed on 300 mm diameter wafers with industry standard equipment.
A porous SiCOH with $k = 2.4$ was investigated in the two integration approaches. RIE was executed on an AMAT Enabler chamber. Thereafter, the original PET is executed on this chamber too.

BDMADMS DSP is executed on an AMAT Axiom chamber, on the same Centura platform. At this Axiom chamber, the BDMADMS bubbler was installed.

The hydrogen peroxide based aqueous wet cleaning was executed on a SEMITOOL Raider SP capsule.

The BDMADMS DSP was investigated on ULK as repair and as new PET approach according to the following characterization methods:

Plasma induced damage was determined employing the hydrofluoric acid (HF) thickness loss (TL) method, described elsewhere [6]. HF was diluted at 1:800 ratio (HF:H$_2$O) and the temperature set at 25 °C. HF TL was carried out on a SEMITOOL Raider SP capsule. Thickness was measured by spectroscopic ellipsometry on a FX100 KLA Tencor.

Open porosity was determined by an ellipsometric porosimeter (EP) from Sopralab using water and toluene as absorbents.

Composition analysis was measured with X-ray photoelectron spectroscopy on a Theta300i ARXPS ThermoFisher equipment.

For the electrical characterization, capacitance and resistance were measured on short loop patterned wafers in designated test structures.

### 3. Results and Discussion

The metrology results focus on the properties of the ULK material after the BDMADMS DSP treatment or intermediate process steps. However, the electrical results were obtained from a complete dual damascene flow, either applying the BDMADMS DSP as repair or as new PET.

#### 3.1 Hydrofluoric thickness loss (HF TL)

In Figure 2, the ULK film thickness loss through diluted HF is illustrated after different processes. The higher damage according to this metrology is induced after the RIE with the current PET. In this case, the surface would be more like SiO$_2$ and SiF$_x$. Because of that, the film will be easily etched by HF. The second highest damage is after the RIE with PET + Wet Cleaning. Both damages are comparable. Comparing the HF thickness loss of RIE without PET + BDMADMS DPS PET (new PET approach) versus the RIE with PET + Wet cleaning + Repair (repair approach), it can be deduced that the new PET approach is significantly lowering the damage.

#### 3.2 Ellipsometry Porosimetry (EP)

On the one hand, looking into the RIE with current PET (Figure 3), the porosity is almost zero after it. It could be due to a more cross linked surface that prevents the absorption of the used absorbents. Interestingly, the wet cleaning provoked an opening of the pores (porosity measured with toluene) and a hydrophilicity increase (porosity measured with water). Thus, the low-k surface was suitably prepared for the repair process. The opening of the pores will improve the diffusion of the repair chemistry into the ULK and the hydrophilicity will accomplish the hydroxyl requirements for the silylation. However, the hydrophobic characteristics couldn’t be recovered after the repair process, indicating not only the presence of hydroxyl groups but also trapping of water after the wet clean. Looking into the porosity measured by water, the BDMADMS DSP PET is keeping the hydrophobic characteristics.

#### 3.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to make a compositional comparison between several elements: carbon, fluorine, oxygen and silicon. Figure 4 shows that after the RIE w/o PET, the low-k material obtained higher carbon and fluorine intensities. Here, a polymer deposited on the ULK surface was detected (Figure 5). However, when the BDMADMS DSP used as PET is processed, the fluorine signal decreased, keeping the carbon signal relatively high. Higher fluorine values could compromise the integrated circuit thermal stability inducing corrosion on the metal barrier. Next, the repair approach is not increasing the carbon signal, which is an indication of an inefficient silylation process. It is believed that, even though the repair was assisted by a wet cleaning, not enough hydroxil groups are present before the silylation mechanism occurs. On the whole, there is no process that restores the carbon signal to pristine values.

#### 3.4 Electrical characterization

For electrical characterization the patterned wafers were processed with 300 mm industry standard equipment. Capacitance and resistance were measured on designated test structures fully passivated by subsequent metal layers. The RIE (with and without PET), electro chemical deposition (ECD) of copper and the chemical mechanical polishing (CMP) processes were executed using conventional processes in GLOBALFOUNDRIES. The wet cleaning, BDMADMS DSP (applied as repair and as new PET) and the barrier-liner and seed deposition were done at IPMS-CNT (Figure 6).

The electrical results are shown in Figure 7. A process of record split (POR) was run as a baseline reference (without BDMADMS DSP). BDMADMS DSP, used as repair and as new PET, decreases the circuit capacitance. The lowest capacitance value was obtained with the new BDMADMS DSP PET approach. However the resistance increased in both cases. In conclusion the RC data of all repair splits is more or less comparable to the POR.

### 4. Summary

According to the used characterization methods, BDMADMS DSP employed as a new PET is offering the following advantages: First, ULK resistance to fluorinated wet clean chemistries is improved (as indicated in HF TL characterization after BDMADMS DSP PET). Second, ULK is preserved with hydrophobic property (proof with EP using water as absorbent). Third, fluorine content was reduced and carbon kept relatively high. Fourth, the bottom and sidewalls of the trenches are treated by the isotropic nature of the DSP.
plasma. Fifth, process time is almost kept constant because the new PET is a replacement of an existing process step. However, the total RC measured on 28 nm node patterned wafers does not show a significant improvement if compared to the POR split. Further investigations with adjusted CD and trench height control are required to assess the full potential of the BDMADMS DSP PET.

ACKNOWLEDGEMENTS

The authors would like to thank many other colleagues working in Fraunhofer IPMS-CNT. The authors would like to thank GLOBALFOUNDRIES for the support. The work was partially supported within the scope of technology development by the EFRE fund of the European Community and by funding from the Free State of Saxony. Project BENGALOS (Project no. 100142950).

REFERENCES


Fig. 1. Repair and new PET approaches, on the left and on the right respectively.

Fig. 2. ULK film HF TL after different processes.

Fig. 3. Open Porosity measured with EP, using toluene (filled columns) and water (empty columns)

Fig. 4. Composition analysis measured by XPS.

Fig. 5. Polymer observed on ULK after the RIE w/o PET.

Fig. 6. Short-loop flow processes.

Fig. 7. POR, BDMADMS DSP PET and BDMADMS DSP REPAIR capacitance and resistance.