A study in interactions of plasmas and wet cleans with ULK materials

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With the implementation of Cu and low-κ dielectrics in back-end-of-line (BEOL), issues arise in every process step that must be addressed. One of the challenges is the susceptibility of Cu and low-κ materials to attack during residue removal (polymer) after low-κ etch and resist strip. This work focuses on the influence of the plasma etch and ash processes on compatibility of porous low-κ dielectrics with a selection of wet chemistries that are used for BEOL polymer removal.

The low-κ material investigated was porous nanocluster silica (NCS), manufactured by Catalysts and Chemicals Industry Corporation (CCIC), which has a dielectric constant (κ) of between 2.3 and 2.4. Prior to wet processing, three groups of plasma processes were applied, (i) ash plasmas: He/H_2 and O_2/CF_4, (ii) etch: $Ar/C_4F_8/CH_2F_2$ @ 60 °C and $Ar/CF_4/CH_2F_2$, and (iii) combination of etch + ash: $Ar/CF_4/O_2/CF_2H_2$ + O_2/CF_4, $Ar/C_4F_8/CH_2F_2$ @ 75 °C + He/H_2, $Ar/CF_4/CH_2F_2$ + He/H_2. The wet chemicals investigated were dilute HF, Chemistry A (organic acids containing, aqueous), Chemistry B (ammonium phosphate containing, aqueous). The wet processing was performed on SEZ Single Wafer Spin Processor 1200. The properties of the low-κ films including dielectric constant were monitored both pre- and post-wet treatment using spectroscopic ellipsometry, contact angle measurement, transmission FTIR spectroscopy, thermal desorption spectroscopy (TDS), and ellipsometric porosimetry with toluene.

Fig. 1 illustrates the change of the κ-value of NCS films after the treatments by various plasmas: He/H_2 does not modify the κ-value significantly while all other plasmas indeed do. Contact angle measurements show that the oxidizing plasmas, such as O_2/CF_4 and $Ar/CF_4/O_2/CF_2H_2$ + O_2/CF_4, turn the NCS surface from hydrophobic to hydrophilic whereas the reducing plasma treatments can maintain the hydrophobicity of NCS films. The change of the contact angle by the various plasma treatments is not in correlation with the change of κ-value, indicating that the damage to the ULK by the plasmas is mainly in the bulk, not only on the wafer surface. The FTIR spectrum in Fig. 3 illustrates that O_2/CF_4 ash plasma results in a higher Si-O-Si bond signal on the surface of the pores, as well as a shift of the network Si-O-Si bond signal compared to the as-deposited NCS, indicating that there is not only chemical modification to NCS films but also structural change. However, He/H_2 only causes a slightly lower Si-O-Si bond signal on the surface of the pores. This indicates that the damage to the NCS film is larger by O_2/CF_4 than He/H_2, which is in good correlation with the k-value change by these two plasmas. As far as the etch and etch + ash plasmas are concerned, similar correlations are observed between κ-value changes and FTIR spectra, indicating that the chemical and structural changes to ULK are the main contributors to the damage. This is confirmed by Fig. 4, which shows the small k-value recovery obtained with a thermal treatment aimed at desorbing moisture and contaminants from plasma-treated films.

The additional changes of κ-value and layer-thickness caused by the wet treatments with dHF, Chem. A, and Chem. B are plotted in Fig. 5 and Fig. 6, respectively. For most NCS films, a dHF treatment results in no significant κ-value change, suggesting that dHF is probably compatible in most cases, with the only exception of $Ar/C_4F_8/CH_2F_2$ + He/H_2 treated film. The thickness analysis shows that the repair of the κ-value by dHF observed in some cases like with $Ar/CF_4/CH_2F_2$ is realized by the removal of the top damaged layer. This is accompanied by etching the pore surfaces and a higher porosity as shown in Fig. 2.

With the only exception of $Ar/CF_4/O_2/CF_2H_2$ + O_2/CF_4 treated film, a Chem. A treatment results in no significant changes of κ-value and layer thickness,

indicating that this chemistry is probably compatible with most NCS films. As far as Chem. B is concerned, the large κ-value change observed on all etch-plasma treated films indicates that this chemistry is not compatible. Indeed, the thermal desorption analysis reveals that salt residues are left in the film after wet treatment, which is probably the reason why a higher k-value is observed.

In summary, a He/H_2 plasma treatment results in no significant κ-value change, while all the other plasmas tested indeed cause damage to NCS films by chemical and structural modification. Absorbed contaminants also contribute to the increase of κ-value but this seems to be secondary.

It is also found that the chemistry selection for wet cleaning is linked with the plasma treatments used for etch and ash. dHF and Chem. A are good chemistries for NCS wet cleaning since they result in either no k-value increase or even do some repair of the low-κ properties. However, Chem. B is not acceptable because salt residues are left after wet treatment, which results in a higher k-value.

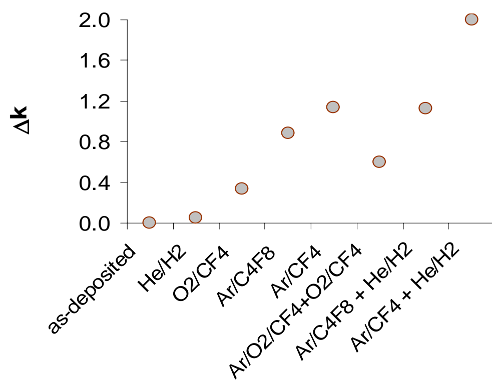

Fig. 1: k-value change by plasma treatments.

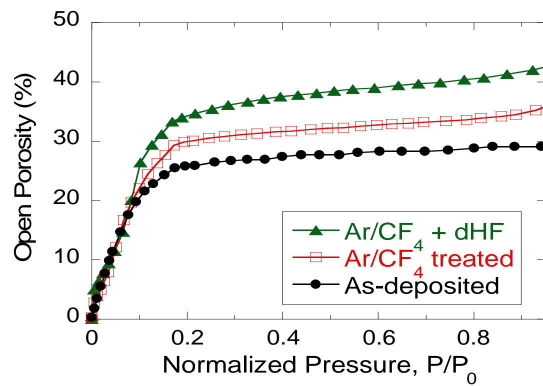

Fig. 2: Porosity analysis for NCS films.

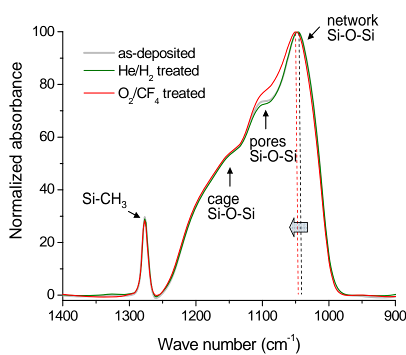

Fig. 3: FTIR spectroscopy for NCS films.

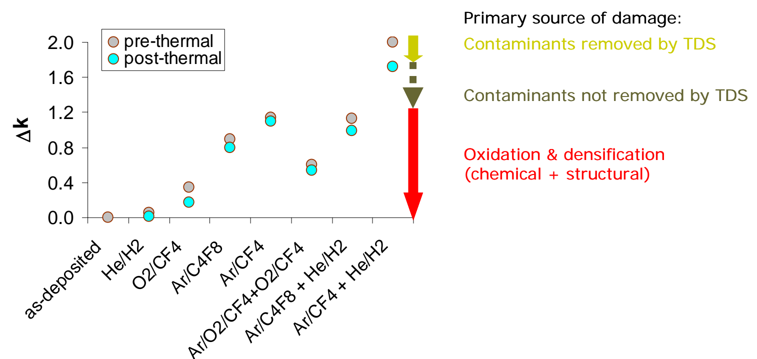

Fig. 4: comparison of k-value change: pre-thermal vs. post-thermal

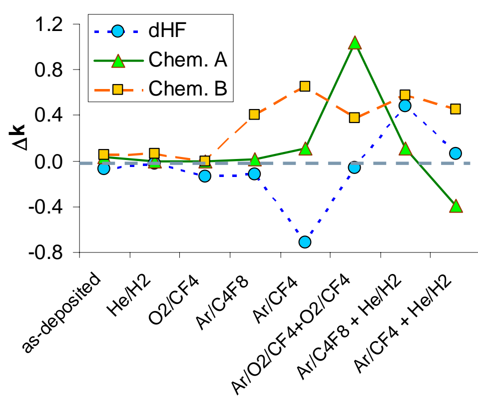

Fig. 5: Additional k-value change by dHF wet treatment

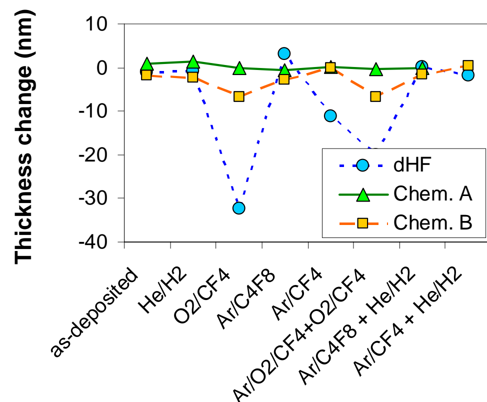

Fig. 6: Layer thickness change by dHF wet treatment