Fabrication of Porogen Residue Free Ultra Low-k PECVD Material by Subsequent High-Afterglow Plasma Treatment and UV Curing

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ABSTRACT

In this work we report a new curing procedure of a plasma enhanced chemical vapor deposited (PECVD) low-k film. The new curing allows us to achieve a mechanically robust and hydrophobic ultra low-k film (k < 3.0). The method is based on a subsequent treatment of deposited films in an afterglow of H2-based plasma and UV assisted thermal curing. The organic porogen removal by the H2-based plasma afterglow with the following UV-curing allows us to produce the porogen-residue-free ultra low-k films with permittivity higher than 3.0 and high elastic modulus of ~ 5 GPa.

INTRODUCTION

The DRAM scaling of ultra-large-scale integrated circuits requires mechanically robust materials with low k-value. Low-k materials recently used in the Cu/low-k integration scheme have k-values between 2.5 and 3.0. One of the limiting factors for further reduction of k-value is mechanical robustness, since major way to decrease k-value is increasing the material porosity. The PECVD low-k deposition of ultra low-k films uses a porogen-based approach. The matrix material is deposited by co-sputtering of alkylsilanes in a plasma-enhanced chemical vapor deposition (PECVD) process. The porogen molecules, usually cyclic hydrocarbons, are introduced into a SiOCH film by co-deposition with the matrix material. To create porosity, the porogen is removed from the thin film using UV-assisted thermal curing. The porogen molecules are photo-dissociated by UV light with the formation of volatile hydrocarbons and nonvolatile carbon-rich residues (porogen residue). The effect of the polymeric residue on optical, chemical and mechanical properties of PECVD films has recently been reported. The mechanical properties as a result of porogen residue removal produce advanced PECVD low-k films (k<3.0) during a photo mask step has been recognized as an integration challenge. Therefore, it is necessary to optimize the curing process of low-k films in order to avoid porogen residue formation. In this work we investigate a new PECVD curing approach that includes two steps. The first step is the complete removal of porogen by thermo-chemical treatment. The second step is improvement of mechanical properties by conventional UV-curing. The porogen removal prior to UV-curing prevents cross-linking of porogen inside the Si-based low-k skeleton. Therefore, subsequent creation of porogen residues in the low-k film skeleton is avoided. However, there is
a narrow process window for selective removal of the C-based porogens from the C-containing Si(111) skeleton. In order to keep the dielectric constant low, the removal of organic-porogen has to be performed without the Si-Cl bond scissions from the SiOCH skeleton of the PECVD deposited low-k material. The removal of organic porogen without skeleton damage (Si-Cl bond scission) is found to be possible by annealing of the low-k films in H₂-based plasma afterglow. The porogen removal efficiency of the H₂ plasma afterglow and its effects on SiOCH films is compared to the conventional UV-curing effect.

EXPERIMENTAL

Materials and experimental procedure. The matrix material was co-deposited with sacrificial porogen by PECVD on 300 mm Si wafers with thicknesses of 65 nm, 120 nm and 190 nm. Then the films were treated with four combinations of the He/H₂ downstream-plasma (DSP) treatments and UV curing: LV, He/H₂-DSP, He/H₂-DSP + UV, LV + He/H₂-DSP. The He/H₂-DSP treatments were performed at a wafer temperature of 250 °C using 350 s of the He/H₂ 20:1 DSP treatment in a 300 mm inlets. The UV-curing was performed in nitrogen ambient at temperature close to 450 °C. The curing procedure was performed using a narrow-band 172 nm UV-source. In order to compare porogen removal efficiency of He/H₂-DSP with the difference wavelengths of UV irradiation, an additional experiment with a broadband UV-source with the wavelengths higher than 200 nm was performed.

Instrumentation. The surface hydrophobic properties before and after the plasma treatments were evaluated using water contact angle measurements (WCA). Optical properties were determined by spectrophotometric ellipsometry (SE) at an incidence angle of 20°. The depth of modification and the optical properties of 190 nm films were estimated using a double layer SE model. The bottom layer was assumed to have optical properties of the as deposited film, while the optical characteristics of the top modified layer were determined by fitting. The mass change related to plasma treatments was measured by mass balance technology on 300 mm wafers (Mettler-Toledo SPS). The open porosity and pore size distributions were evaluated using ellipsometric porosimetry (EPS) [7]. Mechanical properties, Young's modulus and hardness of the low-k dielectric films were measured using a nano indentation XP system (MTS Systems Corporation) with a dynamic contact mode (DCM) and a continuous stiffness measurement (CSM) option under the constant strain rate condition. A standard three-sided pyramid diamond indentor tip ( Berkovich) was used for the indentation experiments. As the indentation tip is pressed into each sample, both depth of penetration (d) and the applied load (F) are monitored.

RESULTS AND DISCUSSION

I. Porogen removal by H₂-based plasma afterglow versus porogen removal by UV-curing.

In order to investigate the removal efficiency of porogen residue in H₂-based plasma afterglow, we studied the effects of 350 s of He/H₂ downstream plasma (DSP) at 240 °C and UV treatments at 350°C on as-deposited PECVD films of 60 nm. After all the treatments the films remain hydrophobic. The water contact angles with surfaces for all the films were approximately 90°.

The results obtained by UV-SPE show that the conventional thermo-assisted UV curing (photochemical) results in creation of porogen residues in contrast to He/H₂-DSP (UV radical treatment). According to the recent results reported by Marsik et al. [8], the absorption bands located between 200 and 300 nm are related to the presence of amorphous-carbon-like porogen residue and porogen. The porogen residues are characterized by absorption band of 4.3 eV (~275 nm) related to the nπ* orbital from C≡C. Therefore, the difference in the absorption spectra of these films is mainly related to different amounts of the porogen or the porogen residues embedded in low-k skeleton.

Figure 1 shows the optical properties of the as deposited matrix-porogen films, the He/H₂-DSP treated film and the UV-cured film. The extinction coefficient of the as deposited film (with porogen) is the highest due to the highest porogen content. The treatments involving He/H₂-DSP results in complete removal of the porogen and porogen residues and the final absorption spectra are becoming similar to the UV spectra of the low-k matrix material [8]. On the contrary, the standard UV-curing processes using narrow band (~172 nm) or broadband (~200 nm) UV-source results in the porogen residues creation. The extinction coefficient has a maximum at 275 nm which marks amorphous-carbon-like porogen residues. Furthermore, the relative changes in reflectance indices of the as deposited film and treated ones are proportional to the porosity increase. The He/H₂-DSP treatments result in the highest RI reduction (the porosity increase) due to efficient porogen removal.
In order to prove that the amount of the organic residues is lower after the HeH₂-DSP than after the UV curing, mass balancemetryology was used. We measured the mass loss of 300 mm wafers with 60 nm films treated with the HeH₂-DSP and/or 172 nm UV, as shown in Figure 2. The cross bars represent the mass measurement error due to backside cleaning. The percentage number reflects approximate mass loss of the films after the treatments. The results show that the conventional 172 nm UV-curing process leaves approximately 46 % more mass in comparison to the HeH₂-DSP treatment. The results agree with the UV-SE data (see the change of the extinction coefficient).

![Graph showing mass loss after UV, HeH₂, and combined HeH₂ + UV treatments](image)

**Figure 2.** The mass loss after UV, HeH₂, and combined HeH₂ + UV treatments as measured by mass balance on 300 mm wafers.

**II. Mechanism and depth of organic removal by HeH₂-DSP plasma.**

We presume that the organic removal mechanism at high temperatures (around 300 °C) is similar to the photo mask removal mechanism in HeH₂-DSP plasma [9]. Heating the low-k in H2-based plasma atmosphere supports the evaporation of the organics residues. Hydrogen atoms promote cracking of the high mass organics or the organics residues, generating smaller CH-preferential chains of lower vapor pressure. However, the organics that need to be removed using HeH₂-DSP are embedded into the porous low-k skeleton. Therefore, the penetration depth of the H radicals into pores low-k skeleton determines the effective depth of organics removal. The penetration depth of the H radicals is limited by their loss in low-k pores as a result of recombination or low-k pore walls or chemical reaction with organics or organics residues. The time-dependent depth of penetration of H radicals for different low-k films was reported in literature [9]. It was found that it saturates logarithmically with time. In order to determine the depth of H radicals' penetration we treated the as-deposited films (with organics) of 190 nm times of 350 s of HeH₂-DSP. Next, we measured the thickness of the organics-depleted layer by UV-SE using double-layer SE model. The depth of organics removal was determined to be about 160 nm. Therefore, the thickness limit to achieve the uniform films using subsequent HeH₂-DSP and UV-curing is about 120 nm - 140 nm. Thicker film fabrication should involve subsequent film deposition combined with HeH₂-DSP curing. The UV-curing should be then performed as a last step due to much higher penetration depth of UV-light (>172 nm) as compared to H radicals.

**III. Effect of combined H₂-based plasma afterlow and UV-curing on mechanical properties of the obtained films.**

In order to study the effect of pore or organics residues on mechanical properties of the obtained films, we measured Young's modulus (YM) and open porosity of the as-deposited film, the UV-cured film and the films after combined HeH₂-DSP and UV treatments. The mechanical properties of the low-k films were evaluated using Nanoindentation (ND) [10]. Since the film thicknesses were relatively small, only a relative comparison was possible due to substrate effect [11].

Figure 3 shows YM versus open porosity. The drop in YM and increase of open porosity after all treatments is due to the pores or the organics residues removal. As we reported previously [5] the HeH₂-DSP treatment of conventionally UV-cured film (UV + He) results in the porosity increase accompanied with mechanical properties reduction due to the organics residues removal. This observation is indicated by the dashed line in Figure 3. However, when the porogen is removed by HeH₂-DSP prior to UV-curing (HeH₂ + UV), the YM of the obtained film exceeds that of the conventionally UV-cured film. The latter observation is indicated by the dotted line in Figure 3. We presume that the porogen removal prior to the UV-curing prevents cross-linking of pores inside the SiOC/H skeleton. Therefore, the subsequent creation of the organics residues inside the low-k film skeleton is avoided. Moreover, the cross-linkage of the mechanically among SiOCH skeleton is not limited by the presence of organic pores residues. Therefore, much stronger Si-O (as compared to Si-CH₂) links are created in the SiOCH skeleton. The Si-O links significantly improve YM of the film.

![Graph showing Young's Modulus vs open porosity](image)

**Figure 3.** The Young's Modulus as measured by Nano-indentation versus open porosity as measured by ellipsometric penetration for as-deposited films and films treated with UV, HeH₂ and combined HeH₂ + UV.
In order to confirm the hypothesis that a porogen residue removal prior to a UV-curing results in a mechanically robust ultra low-k film, we cured the films with varied thicknesses. The as-deposited films with thicknesses of 65 nm, 120 nm, and 190 nm were cured using subsequent HBr:H$_2$:O$_2$ and 172 nm UV cure. The properties of the obtained films are reported in [5]. Two films, with thicknesses of 58 nm and 105 nm, uniform from top to bottom were obtained. In the case of the 190 nm film, the porogen was only partly removed due to the limited penetration of H-atoms as described in section 2.1. The subsequent UV-ohmic annealing of this film results in creation of bi-layer film. Presumably, the transport of decomposed porogen fragments induced by UV-light results in significantly higher film shrinkage as compared to the thinner films (presumably caused by enhanced cross-linkage of the SiOCH matrix). The bi-layer films show even higher YM than the 58 nm and 105 nm films, where the porogen was fully removed. The open porosity and the mean pore radii of 58 nm and 105 nm films were measured by EP. The films have 46 % of porosity and mean pore radii of 1.5 nm. The Young moduli were 5.9±0.82 for the 28 nm film and 5.46±0.31 for the 105 nm film. However, it is necessary to mention that values of YM can be influenced by Si substrate effect [11]. The Si substrate effect might vary depending on film thickness. The YM effect for the 60 and 190 nm PE-CVD films treated with different times of HBr:H$_2$:O$_2$ was found to be 0.82 GPa. The 0.82 GPa higher values were measured for 60 nm films.

Table 1: The properties of achieved films.

<table>
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<tr>
<th>Initial thickness</th>
<th>After HBr:O$_2$ + UV cure</th>
<th>WCA (deg)</th>
<th>k at 100 kHz</th>
<th>YM [GPa]</th>
<th>Open porosity [%]</th>
<th>MFR [mm]</th>
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<td></td>
<td>120</td>
<td>96.15</td>
<td>1.87</td>
<td>5.46±0.51</td>
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<tr>
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CONCLUSIONS

A new curing procedure of enhanced chemical vapor deposited (PE-CVD) low-k films is proposed. The new procedure is performed by conventional UV-curing of PE-CVD film slivers when the porogen is already completely removed. This porogen removal is performed by H$_2$-treated plasma etching at elevated temperature of an as-deposited PE-CVD film. The effective depth of the porogen removal depends on the penetration depth of active H radicals into the porous SiOCH matrix and it found to be approximately 160 nm. The proposed method allows us to obtain the porogen residue-free 58 nm and 105 nm thick low-k films. The obtained films demonstrate high elastic modulus of ~5 GPa, open porosity of 46 %, mean pore radius of 1.5 nm and k-value of approximately 1.8-1.9. The curing of the 190 nm thick film, when porogen was only partly removed, results in mechanically robust bi-layer film with YM of 7.8 GPa and k-value of 2.24.

REFERENCES