Challenges of Plasma Damage of Low Dielectric Constant Materials

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INTRODUCTION

Low dielectric constant (low-k) materials are required as interlayer dielectrics for on-chip interconnects of ultra-large-scale integrated (ULSI) devices to provide high speed, low dynamic power dissipation and low cross-talk noise. Most of low- k films are based on C-doped Silica and Silsesquioxanes and contain 10-15% of organic hydrophobic groups. The hydrophobic groups are needed to avoid moisture adsorption, which increases the effective k-value. The hydrophobic groups are bonded to Si atom in Silica matrix and can be represented as CH_x-SiO_{3/2}, where x ≤ 3. To reach the k-value smaller than 3.0, introduction of artificial porosity is needed. However, porosity creates challenges during the integration of low-k materials in ULSI devices because of diffusion of active species into the film during different chemical treatments, reactive ion etching (RIE), resist strip and cleaning. 1

The damage of low-k films (removal of hydrophobic groups) mainly occurs during the resist strip and cleaning when the low-k film is exposed to O and H based radicals. Further adsorption of moisture leads to degradation of the dielectric constant. We analyze the plasma damage occurring in different plasmas containing O_2, H_2, Ar, He, N_2, and NH_3. The analysis covers a wide range of experimental conditions: ion energy was varied from almost zero to hundreds eV, temperature from 300-1200°C and the pressure from tens mTorr to several Torr. The plasma damage mechanisms and possibility of its reduction are the main subject of discussion. It is demonstrated why the degree of damage can be reduced using He and H_2 based plasmas and elevated processing temperature. Effects of He plasma pre-treatment is also a subject of discussions.

RESULTS AND DISCUSSIONS

The experiments were done with low-k films deposited by Spin-On-Glass (SOG) and Plasma Enhanced Chemical Vapor Deposition (PECVD) technologies. The SOG films had 30% porosity and pore size about 2 nm. PECVD films had porosity close to 25% and pore size of about 1.8 nm. The chemical composition of these films is quite similar. FTIR, XPS and TOF-SIMS (composition and depth profile), Ellipsometric Porosimetry (EP) (porosity and bulk hydrophilicity), contact angle, k-value measurements were used for the evaluation.

The experimental results related to effects of pressure, BIAS and temperature have already been published. 2,3 These data demonstrate that the degree and type of plasma damage depend on chemistry, pressure, temperature and ion energy. An important observation is that the He plasma pre-treatment at moderate temperature (350°C) shows unique effect. This plasma decreases degree of damage during the followed exposure in NH_3 and O_2 based plasmas. Understanding of positive effect of He plasma is based on diffusion-recombination model and properties of EUV emission from He plasma.

Diffusion-recombination model. The diffusion length of gaseous molecules significantly exceeds the film thickness and the observed depth of damage. Therefore, the depth of damage is defined by limited lifetime of active radicals. The depth of damage can be described using so called Thiele analysis, which is widely used in Catalysis. Let’s consider radicals diffusion into single pore with diameter d_p. The depth of damage during the strip is normally less than the film thickness. Therefore, in a certain depth x=L (close to 30-40 nm) C_A=0. The material balance on a differential length of pore is:

\[-\frac{\pi d_p^2}{4} D_1 \left( \frac{dC_A}{dx} \right)_x + \frac{\pi d_p^2}{4} D_2 \left( \frac{dC_A}{dx} \right)_x \approx \frac{\pi d_p^2}{4} \left( \frac{dC_A}{dx} \right)_x \]

The first term of the equation (1) reflects flux into the region x=dx, the second term is a flux out of this region. The third term is radicals consumption inside the region x=dx due to reaction with Si-CH_3 (k_{react}) and recombination (k_{recomb}): k_R=k_{react}+k_{recomb}. Analytical solution of equation (1) shows that the depth of radical penetration depends on ratio of k_R to D_A (\lambda), which is termed as Thiele Modulus (TM):

\[
\frac{d^2 C_A}{dx^2} - \lambda^2 C_A = 0, \quad \text{where } \lambda = \left( \frac{4k_{recomb}}{D_A d_p} \right)^{1/2}
\]

The depth of damage can be reduced if to generate surface active centers increasing the TM value (when k_R>>D_A). It is shown that the k_R value is mainly defined by radicals recombination (k_{recomb}<<k_{react}).

Effect of He plasma. Helium is a light noble gas. Hence the chemical modification of low-k films is excluded. The impact of ion modification is also much less than in gases like Ar, N_2 etc. The modification of low-k material is related to vacuum ultraviolet (VUV) photons emitted by He plasma. The modification of SiO_2 layers caused by VUV radiation from He plasma has been reported in the papers. 4,5 It was shown that VUV light is breaking Si-O bond in SiO_2 and form so called E' defects (oxygen vacancies). UV optical properties of low-k materials are similar to SiO_2 (band gap of SiO_2 and low-k materials are 8.5 eV and 8.0 eV). Silica absorption coefficient is very high below 150 nm. Using the absorption coefficients, one can calculate the penetration depth of VUV photons from He plasma. These calculations show that the intensity of VUV light with wavelength of 60-100 nm decreases to 1/e within the first 10 nm of silica. Therefore, one can conclude that most of photochemical modifications of silica based low-k film are restricted to 20-30 nm of the top layer. This thickness well correlates with XRR data showing densification of the top 17 nm of low-k film. The defects formed by this light are chemically active and are reasons of formation surface active centers localizing recombination of active radicals and other chemical reactions in surface.

In conclusion, the diffusion-recombination model allows describe phenomena related to plasma damage of low-k films. The depth of damage can be significantly reduced by generation of surface active centers increasing the probability of recombination of active radicals. One way to create these centers is VUV photons emitted by He plasma.

References