Self-Grown Hydrophobic Nano Molecule films on the Low Dielectric Materials as an Organic Diffusion Barrier

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To achieve the high performance interconnects with low resistance-capacitance (RC) delay, the integration of low resistivity of metal wiring and low-*k* inter-metal dielectric (IMD) is essential for the next generation ultralarge-scale integrated (ULSI) fabrication. Recently, SiO_2-based dielectric films were investigated as an IMD. Nevertheless, many of the hydrophobic protect groups of the SiO_2-based dielectric materials would be damaged in the photoresist-stripping process. Hydrogen plasma and hydrogen ion implantation post-treatments were used to improve the moisture adsorption behavior on SiO_2-based dielectric materials by the formation of the hydrophobic Si-H bonds. The fast out-diffused H atoms will change the barrier properties of subsequent deposited diffusion barriers. The behavior is called the "nitride effect". In the present work, self-grown nano molecular films (SGMs) on the dry-etched porous methyl silsesquioxane (DE-PMSQ) films were investigated as an organic diffusion barrier by a self-assembly method. The formation mechanism of bottom-up SGMs grown on the DE-PMSQ films is discussed.

720-nm-thick PMSQ samples were coated on the Si wafers by a spin-on method, followed by baking to remove the residual organic solvent of PMSQ films. Dielectric constant of the as-deposited low-*k* PMSQ samples was measured to be 1.82. The low-*k* PMSQ samples were then dry-etched by O_2 plasma in the clustered plasma processing tool. 2% anhydrous diclorodimethylsilane solution ($C_2H_6Cl_2Si$, M.W.= 129 g/mol) was subsequently used to grow SGMs on the DE-PMSQ samples in a closed system at room temperature. Chemical and structural characteristics of the PMSQ films were measured using Fourier transform infrared spectroscope (FT-IR). Refractive index of the low-*k* samples was estimated by using a n&k analyzer. Surface roughness and morphology of the SOMs formed on the DE-PMSQ samples were observed by using atomic force microscope (AFM). Leakage current of low-*k* samples was measured with a metal-insulator-semiconductor (MIS) structure.

After O_2 plasma dry-etching for 5 and 10 min, the specific absorption peaks of Si-C (781 cm^{-1} and 1273 cm^{-1}), and C-H (2975 cm^{-1}) in the DE-PMSQ samples disappeared. Once the Si dangling bonds were formed on the DE-PMSQ by O_2 plasma dry-etching processing, the moisture adsorption on the DE-PMSQ would occur. The value of dielectric constant of the DE-PMSQ samples is 3.82 near the traditional SiO_2 films (3.9). By dipping in the diclorodimethylsilane solution, the specific absorption peaks of Si-C (781 cm^{-1} and 1273 cm^{-1}) and C-H (2975 cm^{-1}) in the DE-PMSQ samples were restored. The reaction was spontaneous at room temperature. It revealed that hydrophobic SGMs (Si(CH3)$_2$) were grown on the DE-PMSQ samples. The dielectric constant of SGM/DE-PMSQ samples decreased to be 2.68, effectively. Even though the hydrophobic SGMs were grown on the DE-PMSQ samples, the surface of SGM/DE-PMSQ was rather smooth by the AFM measurement. In addition, the bonding energy of C-H of SGMs ($(Si\text{-}O)_2\text{-}Si(CH_3)_2$) is 4.14×10^5 J/mol higher than that of Si-H (3.14×10^5 J/mol). Therefore, the C-H bond of ($(Si\text{-}O)_2\text{-}Si(CH_3)_2$) can provide more robust hydrophobic characteristics than that of the Si-H bond. According to the Le Chatelier's principle, the reaction in ultrasonic vibration system was favorable to form SGM on the DE-PMSQ. The overall condensation reaction is summarized by the equation:

$$2Si\text{-}OH_{(sub.)} + Cl_2Si(CH_3)_2 \rightarrow (Si\text{-}O)_2Si(CH_3)_{2\,(sub.)} + 2HCl\uparrow$$

Due to moisture adsorbed on SiO_2-based dielectric materials being a major diffusion path of leakage current, the problem of moisture adsorption in DE-PMSQ films can be decreased by the SGMs. As a result, the leakage current density of SOM/DE-PMSQ sample was lower than that of DE-PMSQ sample. On the other hand, the leakage current density of SGM/DE-PMSQ sample higher than that of as-deposited sample (PMSQ) was seen. It was attributed to the loose arrangement of cage-like Si-O structures (1120 cm^{-1}) of the PMSQ samples destroyed after O_2 plasma dry-etching processing. The result agreed with the observation of FTIR spectra. As a result, using the self-grown nano molecular films as an organic diffusion barrier on the DE-PMSQ can improve effectively the leakage current of SiO_2-based dielectric materials.