Faster conducting speed, higher packing density, and multifunctional chips have been achieved on miniaturized ultralarge-scale integration (ULSI) devices. As the critical dimension of ULSI devices is scaled down to below 180 nm, the major limit to chip performance and reliability is the resistance-capacitance (RC) delay of the metal interconnect, that can be reduced by the replacement of aluminum with copper and the substitution of SiO₂ [dielectric constant (κ) ≈ 4] with low dielectric constant materials. The roadmap for semiconductors industry indicates that the new dielectric materials with κ < 2.7 are required for the device of the sub-130 nm technology node. Various organic polymers, silica sols, and organic siloxanes have been deposited on silicon wafers by dip-coating, spin-on, and chemical vapor deposition (CVD). The nanoporous silica films are synthesized by either aerogel/xerogel process or molecularly templated method. Because of the controllable porosity (45-75%) and uniform diameters in the range of 2-10 nm, molecularly templated mesoporous silica films have been known to provide better mechanical strength and dielectric properties than aerogel/xerogel silica films. After removal of templating organic molecules, silica films are usually rich in silanol groups, which adsorb water molecules easily; therefore, they have to be functionalized to achieve hydrophobicity. Our previous work demonstrated that the hydrophobicity of a calcined silica film can be improved by in situ TMCS silylation of a precursor solution, and hexamethyldisilazane (HMDS) vapor post-treatment. In this work, a systematic study is carried out by varying precursor aging time and TMCS concentration and molecularly templated method. The controlled porosity (45-75%) and uniform diameters in the range of 2-10 nm allow the deposition of mesoporous silica films with smooth morphology as well as steady low dielectric constant and low leakage current density. In addition, the formation mechanism of nanostructured films from TMCS in situ derivatized silica sols was investigated.

**Experimental**

A silica sol was synthesized by refluxing a mixture of tetraethyl orthosilicate (TEOS), H₂O, HCl, and ethanol at 70°C for 90 min. The silica sol and an ethanol solution of P123 were mixed together and aged under ambient condition for 3-6 h, and then TMCS was added under vigorous stirring. The molar ratio of a precursor sol and aged under ambient condition for 3-6 h, and then TMCS was added. The precursor was spin-coated on a pre-cleaned 4 in. p-type Si(100) wafer at 1600 rpm for 30 s. The coating wafer was baked at 80-110°C for 3-6 h, followed by calcination at 400°C for 30 min in an airflow furnace. The precursor solution after adding TMCS was aged at room temperature for 5-150 h. The resulting silica films were treated with HMDS vapor at 150°C for 1 h to passivate residual silanol groups formed after calcination. Fourier transform infrared spectroscopy (FTIR) was used to monitor Si—CH₃ and Si—OH groups in the mesoporous silica film. The surface roughness of the calcined films was characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The thickness of calcined mesoporous silica film was measured by cross-sectional SEM. Thermal desorption mass spectrometry (TDS-MS) was used to study the thermal stability of trimethoxysilyl groups and hydrophobicity of mesoporous silica film. Auger electron spectroscopy (AES) was used to investigate the elementary composition of film samples.

Dielectric properties and leakage current measurements were implemented through the fabrication of metal-insulator-semiconductor (MIS) capacitors. Prior to measurement, the back side of a coated wafer was treated with diluted hydrofluoric acid to remove native oxide, and then coated with aluminum to form a better back contact. An array of aluminum dots was fabricated on the top side of the silica film by thermal evaporation with a shadow mask. A Keithley model 82 CV meter was used to measure the high-frequency capacitance-voltage (C-V) curves at 1 MHz, and dielectric constants of the films were calculated from the capacitance and thickness of the films. The leakage current density of silica films was determined from current-voltage (I-V) characteristics performed on an HP 4156 semiconductor parameter analyzer.

**Results**

**Morphology.**—The surface morphologies of calcined mesoporous silica films prepared with various TMCS concentrations and 4 h aging time are shown in Fig. 1. The surface roughness increases abruptly when the molar ratio of TMCS to TEOS (R) is higher than 0.15. For films prepared by precursors of high R-values, some “islands” of 1-μm round base and 5-9 nm thickness were found on the silica film surface. This is shown in AFM images of samples of R = 0.25 and 0.40 with 4 h aging time (Fig. 1e and f). The islands are composed of SiO₂ as indicated by the peak position and shape of the Si(KLL) Auger signals around 1630 eV (Fig. 2), of which the formation is closely related to the viscosity of precursor solutions. As the aging time increased, a smooth film was obtained, as shown in Fig. 3. The viscosity of the precursors was low (<4.0 cP) and varied with precursor aging time and TMCS concentration, as shown in Fig. 4. A small amount of silicon atoms with an oxidation state less than 4 is probably present in the SiO₂ islands as well, and associated with methylated silicon atoms.

**Electrical properties.**—The sample of R = 0.25 prepared with a silica sol of aging time ~4 h has a high leaking current density (>10⁻⁸ A/cm² at 2 MV/cm). Films obtained from precursor sols with R-value of 0.25 and aging time of 30-150 h exhibit steady dielectric properties over a long shelf life (30 days), and with smooth surface morphologies as shown in Fig. 5 and 6. By preparation with higher TMCS concentration and longer aging time, the silica films possess leakage current density in the order of
10⁻⁹ A/cm² at 1 MV/cm after the HMDS modification, and this leakage current density is stable for at least 30 days (Fig. 6).

Thermal stability of surface hydrophobicity.—TMCS silylation of mesoporous silica films is confirmed by methane desorption in TDS-MS, carbon distribution in AES, and the generation of C—Si bond and reduction of Si—OH vibration intensity in FTIR spectra. The carbon AES depth profile suggests that the carbon is uniformly distributed in mesoporous silica film. Thermal stability of hydrophobicity on the in situ derivatized mesoporous silica films is indicated by the decomposition temperature of methylsilyl groups. Figure 7 shows TDS-MS spectra of calcined mesoporous silica film after exposing to clean room ambient for 1 day. The fragments of m/e = 16 and 18 correspond to methane and water desorptions, respectively. Three water desorption peaks (A1, A2, and A3) have been observed on the mesoporous silica film without TMCS modification, which is similar to that of PECVD SiO₂ film after humidity treatment. The desorption peaks of water associated with surface Si—OH groups are either disappeared or greatly reduced on TMCS-modified mesoporous silica films. According to TDS-MS analysis, films prepared with high TMCS concentration usually exhibit less water desorption. On average, the relative ion intensity of water of the in situ derivatized film is about <30% of that for the underivatized silica film. It means that in situ derivatization effectively reduces water content in mesoporous silica films. A methane desorption signal appears at ~400°C and reaches maximum intensity at 570°C, indicating the thermal stability of surface hydrophobicity up to ~500°C. This observation is consistent with previous FTIR investigation.

Discussion

Silylation of surface hydroxyl groups of porous and nonporous silicon or mixed Si-Al oxides has been known to be an efficient way to alter their surface reactivity and affinity. For mesoporous silica, the fine tuning of hydrophobicity on the internal or external pore surfaces could be achieved by incorporating organic groups through postsynthesis grafting after surfactant removal or co-condensation during surfactant-templated syntheses. The degree of surface silylation is affected by the size of the silylating groups, the pre-outgassing temperature prior to silylation, the pore structure of inorganic silicates, the aging time, and the silylation reagent concentration of the precursor solution. Anwander et al.
demonstrated that the best surface coverage of a silylated MCM-41 was obtained by a silylating reagent with less stereohindrance. To increase the degree of surface silylation, multisteped grafting and pretreatment prior to silylation are usually carried out. The external surface of mesoporous silica is more easily accessible by the silylation reagent. Therefore, through a grafting process, a nonuniform distribution of silylating groups has been observed, and silylating groups are mainly on the external surface of the solids or inside the pore channels but near the channel openings.

Co-condensation with TMCS—By silylation with TMCS, a more uniform surface coverage of silylating groups could be obtained. End-capping the surface hydroxyl groups by $\text{Si}(\text{CH}_3)_3$ may inhibit the self-assembly process of the silica template. This results in mesoporous silica with a wide pore size distribution, in particular with high concentrations of TMCS. Furthermore, the co-condensation with a silylation reagent needs to avoid phase separation in the precursor solution and decomposition of $\text{Si}-\text{C}$ bonds during the late template removing process.

Several mesoporous powder samples were produced previously by co-condensation with cationic surfactant$^{22-26}$ and neutral amine$^{27}$ templated mesoporous silicas. The preparation of mesoporous film by the co-condensation of a silylation reagent with polymer templated silica sol was only reported very recently.$^{10}$ The molecularly templated mesoporous silica film was fabricated by spin-coating on precleaned silicon wafer by using acidic silica sol with P123 and TMCS. In addition to TMCS co-condensation, HMDS silylation has also been employed after calcination to further improve the hydrophobicity of the silica film.

In this work, we have observed that under low TMCS concentration and short aging time, the in situ surface silylation reaction does not interfere with the formation of ordered mesoporous structure (Fig. 1a-c). With high TMCS concentrations, the aging time affects the microstructure of templated silica films, as indicated in Fig. 1c-e and 3. Ryoo and co-workers suggested that the hydrophilic nature of ethylene oxide blocks of the triblock copolymer (P123) is most likely related to the interaction between silica and template as well as the formation of the mesopore-micropore network.$^{28}$ The introduction of TMCS to the precursor solution would reduce the

**Figure 2.** (a) AFM top-viewed picture and (b) AES spectra of the calcined silica film made from the precursor of TMCS/TEOS = 0.25 and aging time 4 h.

**Figure 3.** AFM surface photographs of calcined silica films using in situ derivatized precursor solution with TMCS/TEOS molar ratio of 0.25 and aging time of (a) 4, (b) 30, or (c) 150 h.
degree of the cross-linking of the silica network and suppress the amount of silanol groups on silica species. This, in turn, affects the self-assembly interaction between silica polymers and hydrophilic poly(ethylene oxide) (PEO) of P123, resulting in either the disorder of mesoporous structure or the generation of amorphous silica during the spin coating.

**Plausible mechanism for the silica sol-gel processes.**—After introducing TMCS to a sol of acid-hydrolyzed TEOS and P123, the following reactions may take place:

\[
\begin{align*}
\text{ClSi(CH}_3\text{)}_3 + (RO)_3\text{SiOH} & \rightarrow (RO)_3\text{SiOSi(CH}_3\text{)}_3 + \text{HCl} \quad [1] \\
\text{R:H, C}_2\text{H}_5, \text{Si(OH)}_3, \text{Si(OH)}_2\text{OC}_2\text{H}_5, \ldots & \\
\text{ClSi(CH}_3\text{)}_3 + \text{H}_2\text{O} & \rightarrow \text{HOSi(CH}_3\text{)}_3 + \text{HCl} \quad [2] \\
\text{ClSi(CH}_3\text{)}_3 + \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{C}_2\text{H}_5\text{OSi(CH}_3\text{)}_3 + \text{HCl} \quad [3] \\
\text{HOSi(CH}_3\text{)}_3 + (RO)_3\text{SiOH} & \rightarrow (RO)_3\text{SiOSi(CH}_3\text{)}_3 + \text{H}_2\text{O} \quad [4] \\
\text{C}_2\text{H}_5\text{OSi(CH}_3\text{)}_3 + (RO)_3\text{SiOH} & \rightarrow (RO)_3\text{SiOSi(CH}_3\text{)}_3 \\
& + \text{C}_2\text{H}_5\text{OH} \quad [5]
\end{align*}
\]

The sol-gel process of TEOS includes hydrolysis and condensation. In an acidic media, hydrolysis is faster than condensation, and thus the amount of terminal groups could be higher than that of bridging Si—O—Si groups. This leads to the formation of weakly branched or near-linear silica polymers. At low TMCS concentration, the adding TMCS may react rapidly with silanol groups of linear-type silica polymers for silylation \(\text{Eq. 1}^\text{10}\). At high TMCS concentration, the excess TMCS could also react with water and alcohol in addition to the silanol groups of silica polymers (\(\text{Eq. 2}\) and \(\text{3}\)). The produced \(\text{HOSi(CH}_3\text{)}_3\) and \(\text{C}_2\text{H}_5\text{OSi(CH}_3\text{)}_3\) species can subsequently react with silica polymers, as shown in \(\text{Eq. 4}\) and \(\text{5}\). These silylations can reduce the degree of cross-linking of the silica polymers and weaken the interaction between the silica network and P123. Nevertheless, under high TMCS concentration and long aging time, more terminal Si(CH\(_3\))\(_3\) groups could be formed on intrachannel surface of mesoporous silica. During the aging period, the sol is kept in contact with solvent. The condensation may proceed with alkoxysilanes. When the aging time is not long enough, the polycondensation may not reach equilibrium and thus produce small, \(\text{Si(CH}_3\text{)}_3\) terminated \(\text{SiO}_2\) islands terminated on the film.
preparation from precursor solution with high TMCS concentration and long aging time, hydrophobic mesoporous silica films can be reduced to 1.7-2.1. By optimizing the post-calcination treatments such as further forming gas or reductive plasma treatments to passivate dangling bonds and residual traps on silica films, it is possible to further reduce the \( \kappa \) value of mesoporous silica films to below 1.5.

Figure 7. Thermal desorption of (a) \( \text{H}_2\text{O} \) (m/e = 18) and (b) \( \text{CH}_4 \) (m/e = 16) from the calcined mesoporous silica films synthesized with TMCS and with TMCS/TEOS molar ratios of \( \Delta \) 0.10 or \( \bigcirc \) 0.25 in the precursor solution (heating rate 10°C/min).

Further treatments.—The evaporation-induced supramolecular self-assembly may occur subsequently in seconds after spin coating on the silicon wafer. By using precursors of higher TMCS concentration and long aging time, hydrophobic mesoporous silica films with better dielectric properties have been obtained (Fig. 5 and 6). After the HMDS modification, the dielectric constants of mesoporous silica films can be reduced to 1.7-2.1. By optimizing the post-calcination treatments such as further forming gas or reductive plasma treatments to passivate dangling bonds and residual traps on silica films, it is possible to further reduce the \( \kappa \) value of mesoporous silica films to below 1.5.

According to TDS-MS analysis (Fig. 7), mesoporous silica films prepared from precursor solution with high TMCS concentration typically exhibit better thermal stability of their hydrophobicity. For back-end-of-line (BEOL) process integration in advanced ULSI devices, a trade-off must be made to have reasonable dielectric as well as mechanical properties. Under optimized process conditions, mesoporous silica films with smooth surface morphology could possess a hardness of 1-2 GPa and elastic moduli of 30-60 Mpa.\(^{10} \) Compared with typical aerogel/xerogel silica films with hardness of <1 Gpa and elastic moduli <10 Mpa,\(^{30} \) molecularly templated mesoporous silica films possess better dielectric and mechanical properties which are believed to be related to the ordered microstructure of the films.

Conclusions

In this study, we have proposed a plausible mechanism for the formation of spin-on mesoporous silica film with \emph{in situ} TMCS-derivatized precursor solution. It is likely that the introduction of TMCS in the precursor solution decreases the degree of the cross-linkage of the silica network and suppresses the amount of silanol groups on silica species. The mechanism also shows the effects of both the aging time and TMCS concentration in the precursor solution on microstructure and dielectric property of mesoporous silica films. In order to prepare the silica films with smooth surface morphology and better reliability of dielectric properties, the aging time must increase with the concentration of TMCS in the precursor solution. The \emph{in situ} silylation of a precursor solution with TMCS could improve the hydrophobicity and dielectric properties of mesoporous silica films. The high surface coverage of hydrophobic —Si(CH\(_3\))\(_3\) terminal groups has been observed instead of the hydrophilic Si—OH groups on the calcined surface. The viscosity of a silica sol should maintain a low value, i.e., \( <4.0 \text{cP} \), to avoid the nonuniform thickness of sol-gel films and to produce a mesoporous silica film with steady low dielectric constant. The relatively high decomposition temperature of the hydrophobic units shows that surface —Si(CH\(_3\))\(_3\) groups have a suitable thermal stability for BEOL process integration in advanced ULSI devices.

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