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The preparation of mesoporous silica ultra-low-*k* film using ozone ashing treatment

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Abstract

The ozone ash treatment has been demonstrated to effectively remove the organic template at 200~300 °C as well as to enhance the mechanical strength of mesoporous silica films. The resulting films are of ordered pore structure, strong mechanical strength, and smooth surface. After reacting with hexamethyldisilazane, the silica film has been modified to hydrophobic from hydrophilic and exhibits an ultra-low dielectric constant ($k \leq 2$) and a low leakage current density (10^{-7} A/cm^2) with good electrical reliability.

Keywords: Ozone ashing; Low-*k*; Thin film; Mesoporous silica

1. Introduction

To meet the requirements of 90 nm node technology, materials of dielectric constant (k) value≤2 have been required [1,2]. In order to satisfy this requirement, incorporation of nm-scale pores into the insulated materials has been proposed. However, the porous materials have to face a trade-off between the dielectric constant and mechanical properties. Incorporation of more pores for decreasing the dielectric constant weakens the mechanical strength of films such as Young's modulus and hardness. It is supposed that low-*k* materials with a low mechanical strength have difficulties to endure integrating cycles such as chemical–mechanical polishing, dry etching, and packaging processes [3]. Recently, mesoporous ultra-low-*k* silica dielectric prepared by self-assemble templating synthesis was developed [4–6] and demonstrated to be of better mechanical strength than other nano-porous films [7]. Calcination at a temperature higher than 400 °C to remove the templates was reported to be necessary in the formation of mesochannels in mesoporous materials. It has been known that the Cu/low-*k* interconnect integration should have some integration problems of the thermal copper diffusion and agglomeration of narrow Cu interconnect at a high temperature [8]. It is highly desirable to keep low processing temperature after Cu interconnect formation. In this study, an ozone ashing treatment was employed to remove organic templates and to form nm-scale ordered pore structures in the mesoporous silica films at a relatively low temperature. The ozone treated silica films were characterized and compared with thermal treated film on mechanical strength of Young's modulus and film hardness.

2. Experimental details

A silica sol was deposited by spin-coating on a pre-cleaned 6 inch p-type silicon (100) wafer. The precursor solution was prepared using triblock copolymer Pluronic P-123 (P123) as the organic template [6]. The silica sol-gel was made by refluxing and aging the mixture of tetraethyl orthosilicate (TEOS), P123, H_2O, HCl, and ethanol with a

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composition of TEOS:P123:H_2O:HCl:ethanol=1:0.008~0.03:3.5~5:0.003~0.03:10~34. The solution was spin-coated on the silicon wafer at 1500–2000 rpm under the ambient condition. The as-deposited film was baked at 110 °C for 1 h, and then subjected to an ozone asher at 200 or 300 °C, in which ozone was generated by O_2 flow of 22 slm and N_2O flow of 0.8 slm, and passed through a narrow slit chamber to remove the small amount of organic templates from a thin mesoporous film supported on a Si wafer for 2–5 min. For comparison, a baked film was heated at 400 °C for 60 min in a furnace under a nitrogen flow. The resulting silica films were treated with HMDS (hexamethyldisilazane) vapor at 160 °C to improve their hydrophobicity. Fourier transformation infrared spectroscopy (FTIR) was used to study the chemical bonding in the mesoporous silica films. Surface morphology of the mesoporous silica films was characterized by atomic force microscopy (AFM, Digital Instruments DI 5000). X-ray diffraction (XRD) was used to study the pore nature of the mesoporous silica films. A PHILIPS X'Pert Pro XRD machine using Cu Kα radiation of $\lambda = 1.5406$ Å were employed. The hardness and elastic modulus of the mesoporous silica films were measured by a Nano Indenter XP with a diamond tip in a Berkovich geometry. This technique allows the determination of hardness and elastic modulus depth profiles for depth down to a few tens of nanometers by progressively increasing the applied load from 0.5 to 20 mN. Auger electron spectroscopy (AES, VG Microlab 310F) 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 capacitors. Prior to electric measurements, 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 of 82 CV meter was used to measure the high-frequency capacitance-voltage 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 characteristics performed on an HP 4156 semiconductor parameter analyzer.

3. Results and discussion

FTIR was used to monitor the organic content in the silica films. After 60 min thermal calcination, the template was removed completely, as indicated by the disappearance of the C-H absorption of the organic template (around 2800–3000 cm^{-1}) (Fig. 1). On the other hand, a short period (2~3 min) of the ozone ashing treatment at low temperature efficiently removed the organic species from the film as well, that was detected by FTIR (Fig. 1) and AES analyses (Fig. 2). Because of the active oxygen, radicals produced in the ozone environment may diffuse into the silica film and oxidize the organic template, thereby an ordered porous structure is created. The resulting pore surface is occupied by hydrophilic silanol groups, and can be further modified in HMDS vapor to become hydrophobic [6,7]. The atomic force microscopy (AFM) investigation (Fig. 3) shows that the ozone ashing treatment does not damage the smooth surface of mesoporous silica films. The root mean square surface roughness (Rms) of the 300 °C ozone ashing treated film was estimated to be 0.42 nm, similar to that of the 400 °C thermal treated film (Rms=0.51 nm). Matthew T.J. Keene et al. [9], reported that the elimination of the organic template could be hampered by the steric hindrance of the micropores of zeolites (pore size<1 nm). However, this is not the case for mesoporous SiO_2 of pore diameters in 3~10 nm.

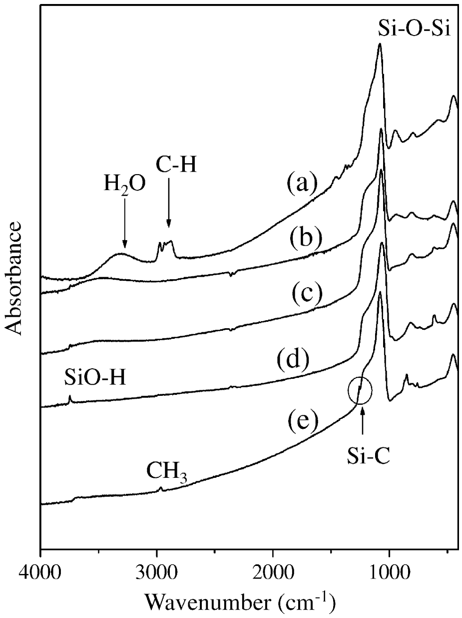

Fig. 1. FTIR spectra of mesoporous silica films after baking (a), and then ozone ashing treatment at 200 °C for 3 min (b), ozone ashing treatment at 300 °C for 3 min (c), or thermal calcination at 400 °C for 1 h (d); compared with a mesoporous silica film treated with baking, ozone ashing treatment at 300 °C and HMDS vapor treatment at 160 °C for 1 h (e).

The anisotropic shrinkage of a film that occurred during various heating processes was measured by X-ray diffraction. The d_{100} spacings of 200 °C and 300 °C ozone ashing samples were found to be shifted from 9.2 nm to 6.6 and 6.2 nm, respectively instead of 5.6 nm for 400 °C thermally treated sample (Table 1). From X-ray reflectivity measurements, the thicknesses of baked, 200 °C, 300 °C ozone ashed and 400 °C thermally treated samples were estimated to be 360, 284, 274 and 261 nm, respectively. These phenomena indicate that the shrinkage in the thickness of a film obtained by ozone ashing treatment is less than that by thermal calcination. The d-spacings ($d_{//}$, or d_{100} for hexagonal symmetry) of pore planes parallel to the substrate

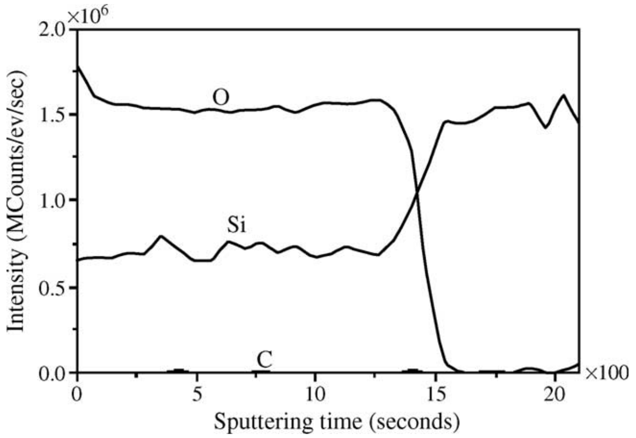

Fig. 2. Auger depth profile of the ozone treated (200 °C for 3 min) mesoporous silica film.

Table 1
Pore nature, mechanical strength and electric properties of mesoporous silica films after ozone treatments for 3 min or thermal calcination for 1 h

Treatment	Ozone		Calcination
	200 °C	300 °C	400 °C
Pore diameter (nm)[a]	4.9	–	5.1
Thickness of pore wall (nm)	1.7	–	1.4
d_{100} (nm)[b]	6.6	6.2	5.6
Young's modulus (GPa)	14.1	17.7	8.4
Hardness (GPa)	0.9	1.1	0.7
Dielectric constant (k value)	2.07	1.95	1.93
Leakage current density (A/cm^2)	6.4×10^{-7}	2.7×10^{-7}	2.1×10^{-7}

[a] determined by the desorption branch of Kr adsorption–desorption isotherms.

[b] determined by θ−2θ scanning XRD.

surface was detected by θ−2θ scan of XRD. To acquire the d-spacing ($d_\perp$) information of pore planes perpendicular to substrate surface, the in-plane XRD measurement was employed and $d_\perp$ values were observed to be almost unchanged after ozone or thermal treatment. The resulting pore symmetry in the cross-section of the mesoporous film was found to change from hexagonal to a 2D centered rectangular after template removing. The average pore sizes of the mesoporous silica films after the ozone treatment and 400 °C thermal calcination were measured by Kr adsorption. Thickness of the pore wall was estimated by assuming mesoporous channels packed in hexagonal symmetry and following the equations of thickness of pore wall = (pore-to-pore distance, a_0) − (pore diameter) and $a_0 = 2 \times d_{100}/\sqrt{3}$, where d_{100} is the d-spacing obtained form θ−2θ scanning XRD. The low temperature and rapid oxidization of the organic template by ozone ashing brought a thick pore wall as listed in Table 1.

Elastic modulus is an important property characterizing the ability of porous materials to withstand stress-induced deformations. For porous materials, the k value decreases with increasing porosity and the mechanical strength will decrease accordingly. However, the mechanical strength of the mesoporous low-k material can be enhanced with the ordered pore structure [7] and thick pore wall. Nano-indentation measurements show that the mechanical strength of the mesoporous silica films has been greatly improved by ozone treatment. Elastic modulus and hardness

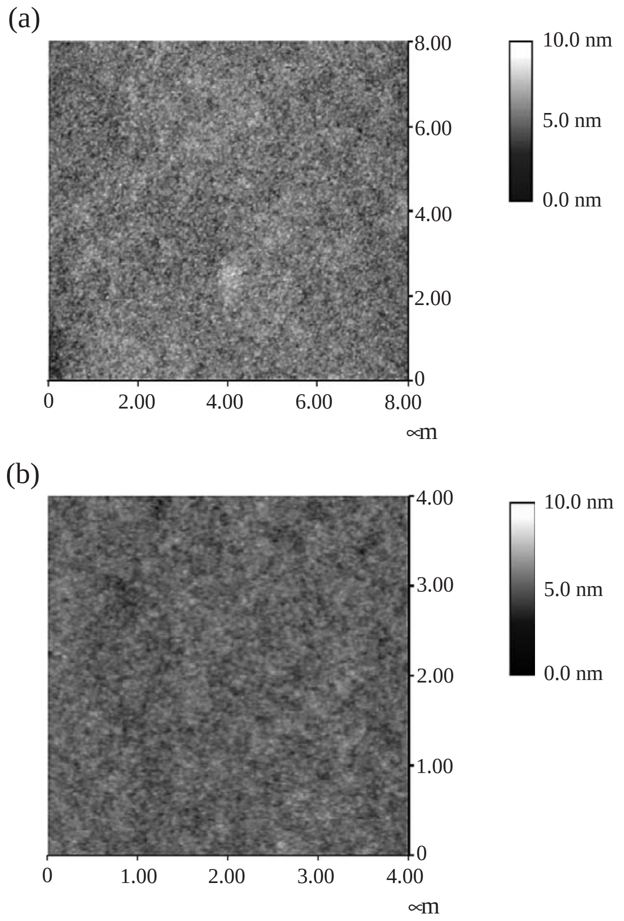

Fig. 3. AFM images of the mesoporous silica film after (a) 400 °C thermal treated or (b) 300 °C ozone-treatment.

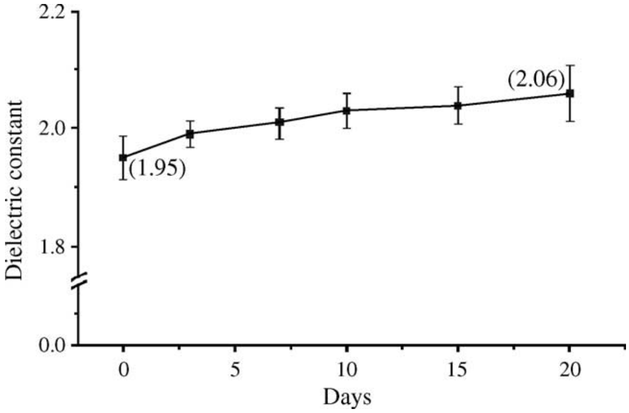

Fig. 4. The variation of dielectric constant values with days for a mesoporous silica film after baking, ozone treatment at 300 °C for 3 min and HMDS vapor treatment at 160 °C for 1 h.

of the mesoporous silica films are listed in Table 1. The mesoporous silica film treated with O_3 at 300 °C for 3 min (Fig. 4) has a Young's modulus and hardness 2.1 times and 1.6 times higher than that of the thermally treated film. Even the sample with ozone treatment at lower temperature (200 °C, 3 min) exhibits a 1.7 times higher Young's modulus and 1.3 times higher hardness than thermal treated one. The exposure to the ozone environment, full of the active oxygen atoms, can remove the organic templated species in mesoporous silica through the attack of atomic oxygen and ozone to form volatile molecules, such as CO_2, H_2O. The values of low dielectric constant and low leakage current density after various treatments on the mesoporous silica film are listed in Table 1. The dielectric constant (k~2) of the mesoporous silica film was observed to be stable for over 20 days, with a slight increase of $\Delta k = 0.11$ in a clean room under ambient conditions. These results can be attributed to the high porosity and the stable hydrophobic property of silica film.

4. Conclusion

The ozone ashing has been demonstrated to be a potential process in the removal of organic template from the mesoporous film and in the integration into the fabrication of low-k mesoporous film for ULSI system.

References

[1] The International Technology Roadmap for Semiconductors (ITRS), Semiconductor Industry Association, 1999.
[2] D. Edelstein, J. Heidenreich, R. Goldblatt, W. Cote, C. Uzoh, N. Lustig, P. Roper, T. McDevitt, W. Motsiff, A. Simon, J. Dukovic, R. Wachnik, H. Rathore, R. Schulz, L. Su, S. Luce, J. Slattery, Proceedings of IEEE Technical Digest on International Electronic Devices Meeting, Washington, DC, USA, 1997 (December 7–10), p. 773.
[3] J.H. Zhao, I. Malik, T. Ryan, E.T. Ogawa, P.S. Ho, W.Y. Shih, A.J. Mckerrow, K.J. Taylor, Appl. Phys. Lett. 74 (1999) 944.
[4] D. Zhao, P. Yang, N. Melosh, J. Feng, B.F. Chmolka, G.D. Stucky, Adv. Mater. 10 (1998) 1380.
[5] H. Fan, H.R. Bentley, K.R. Kathan, P. Clem, T. Lu, C.J. Brinker, J. Non-Cryst. Solids 285 (2001) 79.
[6] C.M. Yang, A.T. Cho, F.M. Pan, T.G. Tsai, K.J. Chao, Adv. Mater. 13 (2001) 1099.
[7] J.Y. Chen, F.M. Pan, A.T. Cho, K.J. Chao, T.G. Tsai, B.W. Wu, C.M. Yang, L. Chang, J. Electrochem. Soc. 150 (2003) F123.
[8] R.A. Donation, B. Coenegrachts, M. Maenhoudt, Microelectron. Eng. 55 (2001) 277.
[9] M.T.J. Keene, R. Denoyel, P.L. Llewellyn, Chem. Commun. 20 (1998) 2203.