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The mechanical properties of hydrophobic nanoporous silica low-k films investigated by utilizing X-ray reflectivity technology

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1. Introduction

To meet requirements of 90 nm node technology, materials of dielectric constant (k) value ≤ 2 have been required. [1] 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 trade-off between the dielectric constant and mechanical properties. Incorporation of more pores for decreasing the dielectric constant weakens 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. Recently nanoporous ultra-low-k silica dielectric prepared by self-assemble template synthesis was developed and demonstrated of better mechanical strength than other nanoporous films. [2] In this work, in-situ trimethylchlorosilane (TMCS) silylation in the sol precursor solution, and a hexamethyldisilazane (HMDS) vapor post-treatment are used to improve the hydrophobicity of the silica films. However, the addition of TMCS in the sol solution disturbs the self-assemble ability and thus influence the mechanical properties of the nanoporous silica films.

The properties of the nanoporous films were studied by the X-ray reflectivity (XRR), Fourier transform infrared spectroscopy (FTIR) and nano-indentation. The applications of XRR technology were investigated as a methodology to determine the thickness and average mass density and to predict the hardness of the nanoporous slica films. This technology does not require the original parameters of thin films. The experimental data of the XRR were compared to the nano-indenter, and the results are demonstrated in this work.

2. Experiments

A porous silica sol was synthesized by refluxing a mixture of tetraethyl orthosilicate (TEOS), H_2O, HCl, and ethanol at 70°C for 90 min. The porous 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 precursor was spin-coated on a 6 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 calcinations at 400°C for 30 min in a nitrogen-flow furnace. The nanoporous silica films were treated with HMDS vapor at 150°C for 1 h to passivate residual silanol groups formed after calcinations. X-ray reflectivity (XRR) is used to study the thickness and average mass density of the nanoporous films. The hardness and elastic modulus of the nanoporous silica thin films were measured by a Nano Indenter XP (MTS Corp.) with a diamond tip in a Berkovich geometry. Dielectric properties and leakage current measurements were implemented through the fabrication of metal-insulator-semiconductor (MIS) capacitors. 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 the silica films was determined from current-voltage (I-V) characteristics performed on an HP 4156 semiconductor parameter analyzer. For easy identification, the untreated, 5%, 10%, and 15% TMCS treated samples were denoted as sample A, B, C, and D, respectively.

3. Results and Discussion

According to the x-ray diffraction (XRD) spectra, as shown in Fig. 1. The θ is the grazing incident angle of the x-ray beam. The strong <100> signal reflects that the sample A has an ordered pore-to-pore spacing of 61 Å after calcinations. In addition, the single <100> peak shows that the pore channel array is lying parallel to the silicon substrate surface. Compared with the sample set without TMCS modification, the TMCS derivatized nanoporous silica films have a weaker and broader <100> diffraction peak indicating a less ordered packing of the nanoporous in the TMCS derivatized silica film. The results suggest that the addition of TMCS in the sol solution significantly degrades the hexagonal pore structure of the nanoporous films. When the TMCS molar ratio increases from 5 to 10%, the <100> diffraction peak shifts to lower diffraction angles from 1.672 to 1.529, and corresponds to an increase in the pore-to-pore spacing from 64 to 70 Å. While the pore space increases with the TMCS concentration, there is no significant difference in the intensity of the <100> diffraction peaks in sample A and B. The diffraction peak of sample D has a 2θangle close to that in sample C, but becomes broad. The presence of TMCS in the sol precursor hampers condensation reactions and perturbs self-assembly of the surfactant micelles,, thus leads to the formation of nanoporous silica thin films with disordered arrangement for the pore network and the silica matrix.

Figure 2 shows the FTIR spectra of the sample A, C and Sample A, C after HMDS treatment for 30 min. Compared with sample A, sample C has a less extent of OH absorption (~3600 cm^{-1}). After treatment with HMDS vapor sample A and C, both nanoporous silica thin films are effectively trimethylsilylated as indicated by the two strong absorption peaks at 1258 and 2965 cm^{-1}, due to $Si-CH_3$ and $C-H_3$ stretching vibration modes, respectively. [2-3] Nanoindentation measurements show that the mechanical strength of the nanoporous films that can be greatly improved by trimethylsilylation after HMDS vapor treatment, as listed in Table 1. An increase in Young's modulus was observed after HMDS hydrophobic treatment. The improvement of mechanical strength can be attributed to the presence of trimethylsilyl groups on the pore surfaces. The mechanical strength of the sample C is weaker than that of the sample A. As discussed previously, a higher TMCS content in the sol-gel precursor solution leads to the formation of a less ordered nanoporous silica network, resulting in weaker mechanical strength. However, the mechanical strength may

enhance after HMDS vapor modification is ascribed to that large terminal trimethylsilyl groups in the nanopore channel surface of the film with a springback effect [2], and thereby compensate for the loss of the mechanical strength caused by the less ordered structure. An HMDS vapor treatment can furthermore effectively modify the hydrophobicity of the nanoporous silica. The dielectric constant decreases to 1.76, and the leakage current density reduces to $8.7x10^{-8}$ A/cm^2 for 10% TMCS sample.

Figure 3 shows the XRR data from nanoporous films after varying process conditions. The position of the first kink in each curve corresponds to the critical angle θc for the nanoporous films and the second kink corresponds to that of the Si substrate. Moreover, the reflectivity drops sharply as the x-ray beam begins to penetrate the film after a critical angle. The critical angle of the nanoporous film is related to the real component of the refractive index δ by $\cos(\theta c) \approx 1-\delta$ from the Fresnel equations. [5] For a given film $\delta \sim \rho_e \lambda^2$, where ρ_e is the number of electrons per unit volume in the film, and λ is the wavelength of the x ray. The film mass density can be obtained from the number of electrons per unit volume in the film. In figure 3, the critical angle of the concentration of TMCS is obtained. The result displays the average mass density of the films decrease with increasing concentration of TMCS in precursor solutions.

4. Conclusion

Microstructural and mechanical properties of nanoporous silica films have been studied by XRR, XRD, FTIR, and Nano indentation. Compared with other porous low-k dielectrics, the self-assembled molecularly templated nanoporous silica films demonstrate better mechanical properties. This is ascribed to the presence of a well-ordered pore channel structure in the nanoporous silica films. When the TMCS is added in sol precursor solution, the nanoporous films have a weaker mechanical strength. The pore channel structure of the nanoporous silica film becomes disordered arrangement for the TMCS derivatized nanoporous films. Furthermore, FTIR analysis reveals that the chemical structure in the solid matrix of the porous network of the TMCS derivatized films is more disordered than those without TMCS modification. Trimethylsilylation by the HMDS vapor treatment can significantly improve the mechanical strength of the nanoporous silica thin films. The XRR and nanoindentation measurement results can be explained in terms of the pore microstructure of the nanoporous silica network and the springback effect due to the presence of trimethylsilyl groups in the nanoporous films.

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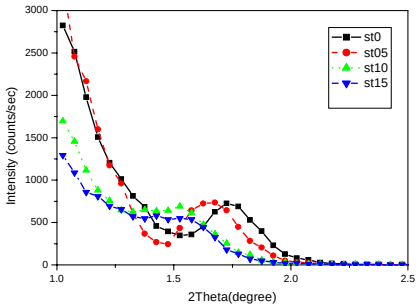

Figure 1 X-ray diffraction spectra of the calcined nanoporous silica films with 0 % (sample A), 5 % (sample B), 10 % (sample C) and 15 % (sample D) in different TMCS concentration

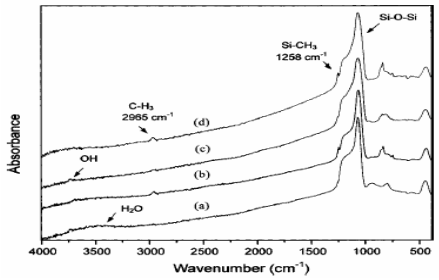

Figure 2 FTIR spectra of nanoporous silica thin films; (a) as-calcined film, (b) as-calcined film after HMDS treatment for 30 min, (c) as-calcined TMCS (10% molar ratio) derivatized film, (d) TMCS derivatized film after HMDS treatment for 30 min.

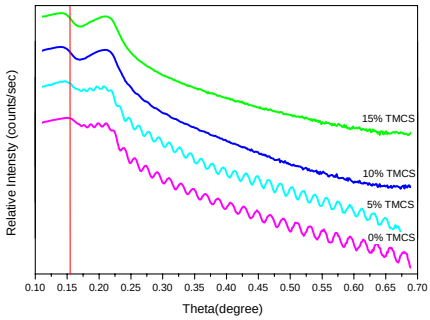

Figure 3 X-ray reflectivity (XRR) spectra of the samples A, B, C, D

Table 1. The material properties of nanoporous silica thin films. Sample C' is TMCS (10% molar ratio) derivatized film after HMDS treatment for 30 min.

Sample	Dielectric Constant (A-C) samples +HMDS	Leakage current density (A/cm2) (A-C) samples +HMDS	Film Thickness (Å)	Critical Angle	Young's Modulus	Hardness
A	1.94	$2.6x10^{-7}$	2643.73	0.1536	10.6	0.47
B	1.84	$1.1x10^{-7}$	2962.03	0.1486	8.7	0.39
C	1.76	$8.7x10^{-8}$	3258.	0.1423	7.2	0.34
C'	----	----	----	----	9.3	0.68