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The improvement of mechanical and dielectric properties of ordered mesoporous silica film using TEOS–MTES mixed silica precursor

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Abstract

Due to the rapid decrease in physical dimension of today's devices, lower resistive metal and/or lower dielectric constant material have to be applied. Recently, ordered mesoporous silica film has been drawn an attention for low-*k* application due to its ordered pore structure. However, it has been more required that low-*k* dielectrics should have low leakage current, high breakdown strength and high mechanical stabilities. In this study, ordered mesoporous silica films were prepared by sol–gel process using tetraethylorthosilane and methyltriethoxysilane as a mixed silica precursor in order to increase the mechanical and dielectric properties. It was found that the properties of the films were improved when the pore ordering and the amount of the incorporated methyl ligand were maximized.

Keywords: A. Sol–gel process; D. SiO_2; E. Insulators; Brij-76

1. Introduction

The reduced dimension and increased integration in ultralarge scale integrated (ULSI) devices cause an increased resistance on back end of the line (BEOL) metallization and increased interlevel and intralevel capacitances, which cause an increased signal delay [1,2]. Low dielectric constant films in ULSI devices are required to reduce power dissipation, propagation delay, and cross-talk noise of the interconnect structure. It is generally accepted that extendibility to the region of ultralow dielectric constant cannot be attainable without introducing the concept of porosity because air possesses the lowest dielectric constant of 1 [3]. Among the various low-*k* porous materials, porous silica films are most promising due to their superior mechanical strength, thermal stability and most importantly, compatibility with silicon wafers and the related materials that are used in existing IC technology. The very attractive process for synthesizing porous silica films is the sol–gel process, which easily enables control of the dielectric constant. Among the sol–gel derived porous silica films, ordered mesoporous materials have been widely investigated for low dielectric film applications [4,5]. In the synthesis process of ordered mesoporous material, evaporation-induced self-assembly (EISA) enables the formation of highly ordered mesoporous silica films of various pore structures [6]. Our group reported that the ordered mesoporous silica film with a Brij-76 ($C_{18}H_{37}(OCH_2CH_2)_{10}OH$) block copolymer shows appropriate mechanical and electrical properties [7,8].

A framework modification through the incorporation of an organic functional group can lower the dielectric constant of the porous silica film due to low polarizability of organic group. Furthermore, it can reduce adsorption of vapor due to its hydrophobic property [9]. Generally, organically modified, ordered mesoporous silica films have been prepared using $RSi(OEt)_3$ ($R = CH_3$, C_2H_5, and C_8H_7) and tetraethylorthosilane (TEOS) as a hybrid framework source and surfactant as a template.

In this work, methyltriethoxysilane (MTES) was used as the mixed silica precursor with TEOS and the mechanical and dielectric properties of the films were investigated according to the mixing ratio of MTES and TEOS. As a result, the composition for the ordered mesoporous silica film could be optimized. Furthermore, the mechanical and dielectric properties of the film were investigated for low-*k* applications.

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2. Experimental procedure

Ordered mesoporous silica films were synthesized as follows. First, EtOH as a solvent and acetone as a cosolvent were mixed. Acetone was added because it can bring structural stability by reducing the condensation rate due to its aprotic property [8]. Brij-76 block copolymer was dissolved in mixed solvent and then acidified H_2O was added. After stirring for 1 h, TEOS and MTES as silica precursors were separately added to the solution. The final composition of MTES:TEOS:acetone:EtOH:H_2O:HCl:-Brij-76 was x:(1 − x):8:12:5:0.01:0.05. The molar ratios, x was varied from 0 to 0.3. After aging time for 30 min, each sol was spin-coated at 3000 rpm for 30 s at 23 °C in relative humidity of 30 %. Organically modified, ordered mesoporous silica films could be fabricated by removing the block copolymer at 400 °C with a heating rate of 2 °C/min.

For the investigation of ordered pore structure, X-ray powder diffraction (XRD) patterns were collected using Cu Kα radiation with wavelength of 1.5418 Å and a transmission electron microscopy (TEM) with 200 kV of acceleration voltages was used to get a cross-sectional image of the specimen. Porosity of the silica film was calculated by measuring ellipsometry with a He–Ne laser source of 632 nm wavelength [10]. Fourier transform infrared (FT-IR; Jasco 300Z) spectroscopic analysis was performed to reveal the chemical species of the silica wall. The mechanical properties of the ordered mesoporous silica film were investigated by continuous stiffness measurements using a MTS nanoindentor XP [11]. This allows for a continuous measurement of elastic modulus and hardness even for extremely thin-layered materials. For electrical property measurements, circular Al dots were deposited on the ordered mesoporous silica films as an electrode using a thermal evaporator. Aluminum was also deposited on the backside of the Si wafer for ohmic contact. After deposition, post-metal annealing was performed by rapid thermal annealing at 300 °C for 1 min. Capacitance–voltage (C–V) characteristics in the metal–insulator–semiconductor structure were obtained using an HP 4280A impedance/gain-phase analyzer at 1 MHz.

3. Results and discussion

In case of mixed silica precursor of TEOS and MTES, ordered mesoporous silica film can have the pore structure of 2D hexagonal or body-centered cubic according to the MTES molar ratio, namely, ratio of MTES/(TEOS + MTES) [12,13]. When its ratio belongs to the region between 0.1 and 0.2, the pore structure is 2D hexagonal structure, and when the ratio is 0.25, the pore structure is body-centered cubic structure. But when the ratio exceeds 0.3, the pore structure is collapsed [12]. Generally, 3D pore structure is stronger mechanically than 2D pore structure [14]. Therefore we focused on the ordered mesoporous silica film having the body-centered cubic pore structure which is formed at the region where MTES molar ratio is 0.2–0.3.

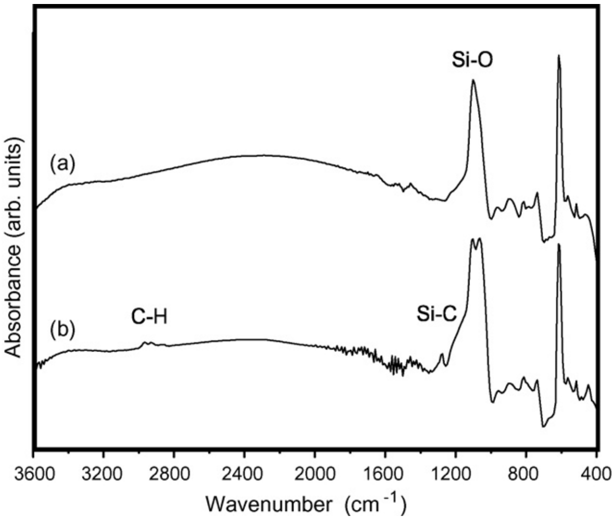

Fig. 1. FT-IR spectra of the ordered mesoporous silica film made from (a) TEOS silica precursor with composition of 1 TEOS:20 EtOH:5 H_2O:0.01 HCl:0.05 Brij-76 and (b) MTES–TEOS mixed silica precursor with 0.27 MTES molar ratio.

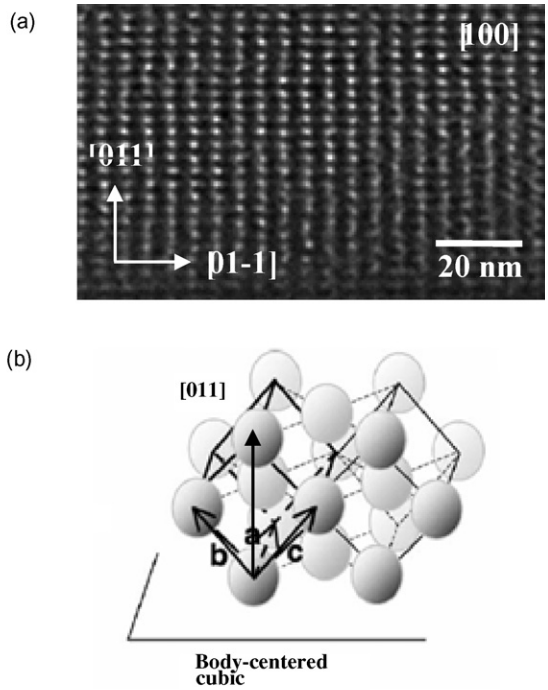

Fig. 2. (a) TEM image of the ordered mesoporous silica film with zone axis of [1 0 0] and (b) schematic image of body-centered cubic pore structure when (0 1 1) is substrate-parallel plane.

In order to confirm the silica wall modification with the MTES precursor, FT-IR spectra analysis was performed. The ordered mesoporous silica film without MTES addition, which was investigated in our previous work, is shown in Fig. 1(a) and the ordered mesoporous silica film with MTES mixing ratio of 0.27 is shown in Fig. 1(b) [15]. In Fig. 1(a) and (b), the intense absorption peak of Si–O bond is located at 1060 cm^{-1} due to the vibration of Si–O–Si linkage. In Fig. 1(b), the additional peaks were shown due to silica wall modification. The peaks located at 1277 cm^{-1} and 2975 cm^{-1} are assigned to the Si–C bond and –CH_3 unit, respectively [16]. From the above

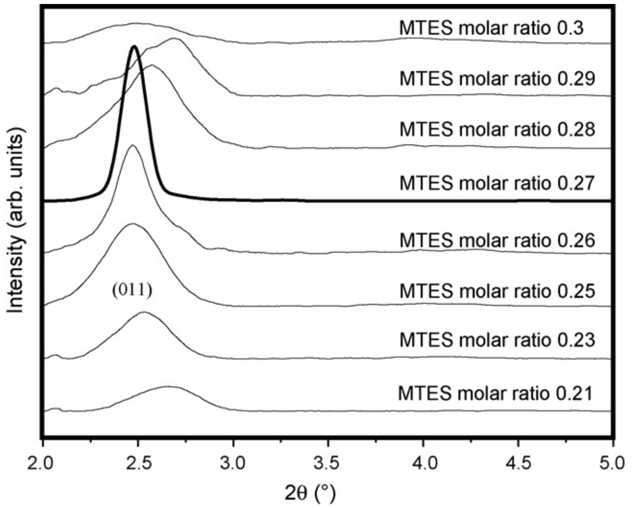

Fig. 3. XRD patterns of the ordered mesoporous silica film with the variation of MTES molar ratio.

analysis, it could be concluded that silica wall was successfully modified with Si–C bond.

Fig. 2(a) shows TEM image of the ordered mesoporous silica film. In this TEM image, zone axis was [1 0 0], and the direction normal to substrate was [0 1 1]. From Fig. 2(a) it could be observed that pores were well-ordered. The pore structure is a distorted body-centered cubic with anisotropic shrinkage for the normal direction to the film surface, where (0 1 1) plane is parallel to the substrate. The schematic image was displayed in Fig. 2(b).

Fig. 3 shows XRD patterns of the ordered mesoporous silica film with the MTES molar ratio. In this XRD patterns, the most intensive peak was (0 1 1) plane diffraction peak of body-centered cubic pore structure. As the MTES molar ratio increases up to 0.27, (0 1 1) diffraction peak intensity increases. This result means that body-centered cubic pore structure was formed gradually with increase of MTES molar ratio more than 0.2. However, as the MTES molar ratio increases over 0.27 MTES molar ratio, the degree of ordering decreases gradually. And finally, at 0.3 MTES molar ratio the (0 1 1) diffraction peak of the body-centered cubic pore structure was disappeared. It is caused by the collapse of the pore structure, due to too high MTES concentration in the silica sol [12]. Because the condensation rate of MTES is seven times faster than that of TEOS, high MTES molar ratio results in excessive condensation before spin-coating of silica sol [17]. Therefore, the ordered packing of the micelle is disturbed by the excessively condensed silica oligomer, and so the pore structure becomes disordered. Conclusively, when MTES molar ratio is 0.27, the mesoporous silica film has the highly ordered pore structure.

Fig. 4 shows porosity variation as a function of MTES molar ratio. According to increase of MTES molar ratio, the porosity of the ordered mesoporous silica film increases overall. It is caused by Si–C bonds in the silica sol. Because of MTES addition, Si–C bonds were formed in the silica sol. These bonds reduced the repulsive force between the silica oligomers. If the repulsive force is reduced, the geometric factor becomes higher. The high geometric factor makes the micelle size larger [18]. The pore size becomes larger due to larger micelle, and so the porosity of the ordered mesoporous silica film increases as MTES molar ratio increases [19]. When MTES molar ratio is

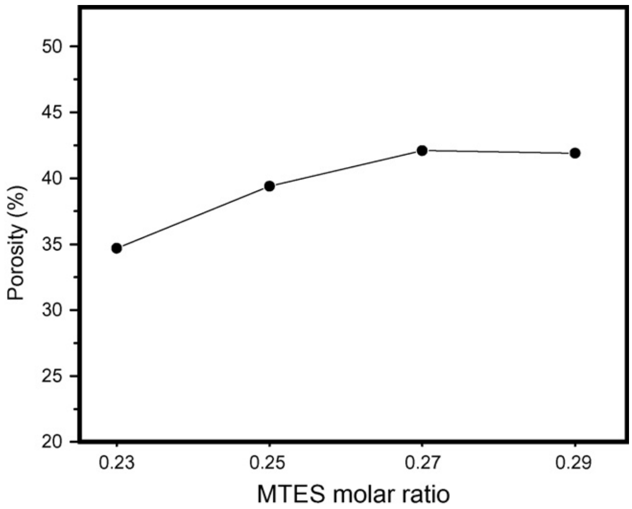

Fig. 4. Porosity variation for the ordered mesoporous silica film as a function of MTES molar ratio.

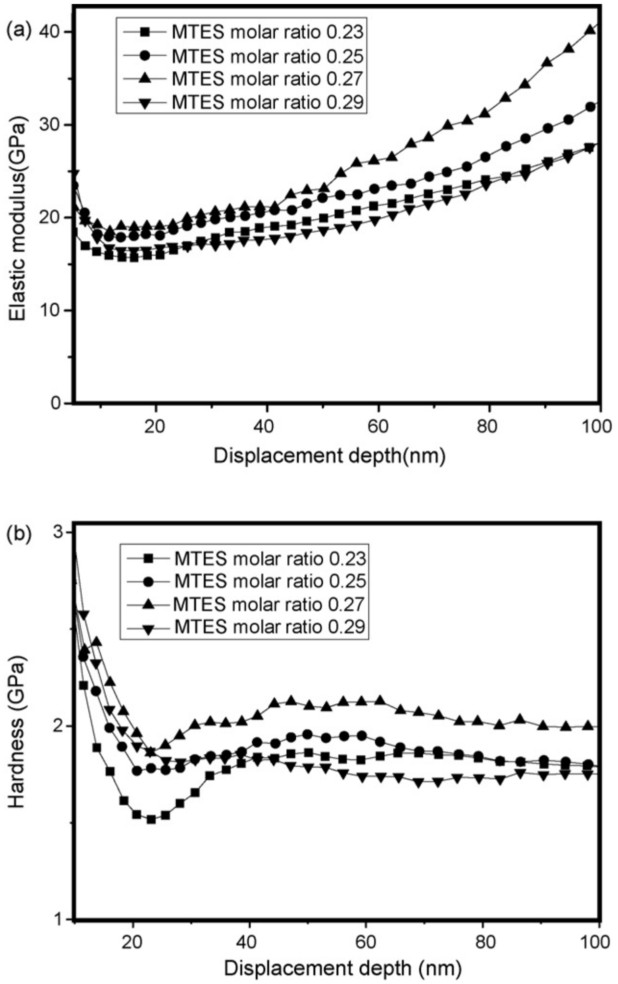

Fig. 5. (a) Elastic modulus and (b) hardness of the ordered mesoporous silica film with the variation of MTES molar ratio.

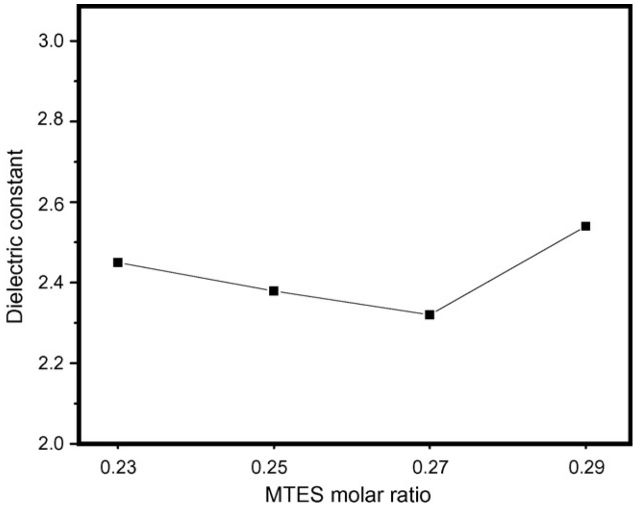

Fig. 6. Dielectric constant of the ordered mesoporous silica film with the variation of MTES molar ratio.

0.27 and 0.29, their porosities are similar. That porosity does not increase at 0.29 MTES molar ratio is caused by the degree of ordering. Over 0.27 MTES molar ratio, the degree of ordering decreases as shown in Fig. 3 and the collapse of the pore structure starts by degrees. This collapse lowers the increased porosity according to the increase of MTES molar ratio. After all, the porosity at 0.29 MTES molar ratio becomes similar to 0.27 MTES molar ratio.

Fig. 5(a) and (b) shows the mechanical properties of the ordered mesoporous silica film with the variation of MTES molar ratio. Both the elastic modulus and hardness increase as MTES molar ratio increases up to 0.27 and then decrease. The mechanical properties of porous silica film are largely dependent on its density. Generally, the mechanical properties are decreased according to the decrease of density. The density of porous material becomes low as the porosity increases. However the property of pore structure, such as the degree of ordering and silica wall thickness, also affects the mechanical properties of the films. This is because the ordered pore structure with adequate wall thickness can disperse the mechanical force into whole structure uniformly without concentration of some specific parts. As shown in Fig. 3, the degree of ordering of pore structure increases until 0.27 MTES molar ratio and then decreases according to the increase of MTES molar ratio. Through the tendency correspondence of the ordered degree and the mechanical properties, the relationship between them is proved.

Fig. 6 shows the variation of dielectric constant of the ordered mesoporous silica film with the change of MTES molar ratio. The dielectric constant decreases as MTES molar ratio increases up to 0.27. This is explained by two aspects, the porosity and the existence of Si–C bond. The dielectric constant of air is nearly 1. The high air fraction in the porous silica film makes the dielectric constant of the film low. Therefore the higher the porosity is the lower dielectric constant the film has. Also, Si–C bond formed by MTES addition has lower polarizability than Si–O bond [20]. As MTES molar ratio increases, the amount of Si–C bonds in the silica film increases. Besides, Si–C bonds as well as $-CH_3$ unit change the surface property from the hydrophilic to hydrophobic. The hydrophobic surface plays a role in disturbing the vapor adsorption which is the cause of the leakage current and the restrain of low dielectric constant. Therefore the silica film having hydrophobic property exhibits better dielectric property. The dielectric constant becomes lower with the increase of MTES molar ratio. Over 0.27 MTES molar ratio the increase of the dielectric constant is observed. It is caused by the decrease of porosity over 0.27 MTES molar ratio. The dielectric constant of the ordered mesoporous silica film of 0.27 MTES molar ratio is 2.32. Based on Figs. 5 and 6, the ordered mesoporous silica film of 0.27 MTES molar ratio has better dielectric property as well as the mechanical properties. This means that the optimized film synthesized in this work satisfies the requirement for low-*k* dielectric of ULSI device as aspects of the dielectric and mechanical properties.

4. Conclusions

The ordered mesoporous silica film was synthesized successfully using TEOS–MTES mixed silica precursor. By controlling mixing molar ratio between MTES and TEOS, highly ordered mesoporous silica film could be synthesized. In the region of MTES molar ratio having the body-centered cubic pore structure, 0.2–0.3, it was investigated that the silica film of 0.27 MTES molar ratio has the most ordered bcc pore structure. Because of the high degree of ordering, the silica film could have the superior mechanical properties. Also because of high porosity and Si–C bond, the silica film could have better dielectric property. Dielectric constant of the ordered mesoporous silica film synthesized from the optimized sol composition is 2.32. Conclusively, highly ordered pore structure with Si–C bond makes dielectric constant lower and mechanical properties stronger, and it can satisfy the requirement for low-*k* dielectric of ULSI device as aspects of the dielectric and mechanical properties.

Acknowledgements

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