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Citation: *Journal of Vacuum Science & Technology B* **23**, 2034 (2005); doi: 10.1116/1.2050656

View online: <http://dx.doi.org/10.1116/1.2050656>

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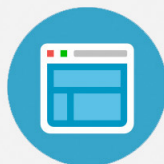
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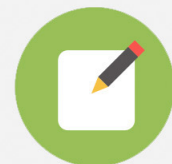


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Thermal stability of trimethylsilylated mesoporous silica thin films as the ultralow- k dielectric for copper interconnects

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(Received 19 May 2005; accepted 8 August 2005; published 14 September 2005)

Surfactant templated mesoporous silica thin films were prepared as the intermetal dielectric for ultralarge scaled integrated circuit application, and the thermal and chemical stability of the Cu/nitrided Ta/mesoporous silica film stack on the Si wafer was studied. Trimethylsilylation of the mesoporous silica thin film by hexamethyldisilazane vapor treatment significantly improves hydrophobicity of the mesoporous dielectric, and a dielectric constant (k) smaller than 2 can be obtained for the thin film. According to Fourier transform infrared spectroscopy and thermal desorption spectroscopy, decomposition of trimethylsilyl groups on the pore surface becomes significant at temperatures larger than 400 °C. However, when the metallized film stack was annealed at temperatures higher than 400 °C, the film stack shows little delamination between layers and still retains smooth interfaces according to Auger electron spectroscopy and transmission electron microscopy analyses. Ta₂C nanoparticles were found to exist at the Ta(N)/mesoporous silica interface of the film stack annealed at 600 °C. Bias-temperature stress test of the metallized film stack shows little Cu diffusion into the mesoporous dielectric layer. © 2005 American Vacuum Society. [DOI: 10.1116/1.2050656]

I. INTRODUCTION

The International Technology Roadmap for Semiconductors (ITRS) has proposed that the copper interconnect process requires an intermetal dielectric (IMD) with a bulk dielectric constant ($k_{\text{bulk}} < 2.4$ for the 70 nm integrated circuit (IC) technology node in 2007.¹ The urgent need to seek an ultralow- k dielectric material for future IC technology nodes has brought extensive attention to porous dielectric materials. Because air has a dielectric constant close to 1.0, introducing air into a dielectric can reduce the k value of the material as a whole. Therefore, in order to reduce the k value of a dielectric, it is a logical strategy to decrease the mass density of the dielectric, or introduce pores in the dielectric.²⁻⁴ Because of possessing a high porosity, mesoporous dielectrics have a very low k value, and are considered as a potential candidate for IMD materials for sub-65 nm technology nodes. However, the high porosity brings in many hurdles to porous ultralow- k dielectrics when integrated into the Cu damascene process. Many process steps, such as dry etching, wet cleaning, and chemical mechanical polishing, are viciously impacted by the pore structure of the porous dielectric.

Among various porous ultralow- k dielectrics, silica-based mesoporous materials are widely studied because they are chemically compatible with contemporary IC processes and

a $k < 2.5$ can be easily obtained owing to a high porosity. However, the mechanical strength of porous silica dielectrics is far inferior to that of a conventional silicon oxide IMD. Moreover, porous silica dielectrics prepared by the sol-gel method are usually hydrophilic, and thus moisture uptake can seriously degrade the dielectric stability of the porous materials. Porous silica thin films with a nanoscaled pore size, such as xerogel⁵⁻⁷ and surfactant templated mesoporous silica,⁸⁻¹⁰ are generally fabricated by the sol-gel method. In previous studies we have successfully prepared surfactant templated mesoporous silica thin films with a k value < 2.0 .^{10,11} In order to keep a stable dielectric property, the hydrophilic mesoporous silica thin film has received trimethylsilylation treatment, which was accomplished by exposing the as-calcined mesoporous silica thin film to the hexamethyldisilazane (HMDS) vapor.¹⁰⁻¹³ The HMDS vapor treatment introduces trimethylsilyl terminal groups on the pore surface of the mesoporous silica dielectric. It not only improves hydrophobicity, but also enhances the mechanical properties of the mesoporous silica thin film.¹² However, insertion of trimethylsilyl groups on the pore surface introduces the uncertainty of thermal stability of the mesoporous thin film. Having high thermal and chemical stability is certainly crucial to the mesoporous silica dielectric to be integrated into the copper interconnect process. But the organic trimethylsilyl group can only withstand up to a certain temperature limit in thermal treatments, and may be decomposed during various high-temperature IC processes, thus leading to devastating

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damage to the interconnect structure. In this work, the thermal and dielectric stability of the HMDS-treated mesoporous silica thin film was studied, and its impact on the Cu-metallized mesoporous silica film stack will be discussed.

II. EXPERIMENT

The preparation method of the mesoporous silica thin film has been described previously.¹⁰ A silica precursor sol was prepared by mixing and refluxing a solution of tetraethyl orthosilicate, H₂O, HCl, ethanol, and a nonionic surfactant, Pluronic P-123 (P123). The precursor was spin coated on precleaned 4 or 6 in. (100) *p*-type silicon wafers, followed by baking at 80–110 °C for 1 h to remove the aqueous solvent. The organic template molecules were removed from the mesoporous silica film by calcination at 400 °C for 30 min in a furnace with air flow. The mesoporous silica thin film had an average pore size of ~3–4 nm and a porosity of ~50%.¹⁰ Hydrophobicity of the as-calcined mesoporous silica film can be significantly enhanced by exposing the porous dielectric film to HMDS vapor at 165 °C. In order to study the thermal stability of the Cu-metallized mesoporous silica film, a film stack with the layer structure, SiN_x/Cu/Ta(N)(30 nm)/mesoporous-SiO₂ (200 nm)/SiO₂ (20 nm), was deposited on the *p*-Si wafer and annealed in N₂ ambient at various temperatures. Partially nitrated Ta was sputter deposited on the mesoporous silica layer as the Cu diffusion barrier in a sputtering system (SBH-3308RDE, ULVAC Taiwan Inc.) at a power of 500 W. The base pressure of the sputter chamber was $<6 \times 10^{-7}$ Torr. During the Ta(N) deposition, a gas mixture of Ar and N₂ was used for Ta nitridation with the gas flow ratio Ar:N₂=1:0.05. The Cu film 300 nm in thickness was then deposited on the Ta(N) layer at a power of 1500 W in the same sputtering chamber without breaking the vacuum. The thin silicon nitride was deposited on the Cu layer by plasma enhanced chemical vapor deposition (PECVD) at 250 °C to protect the underlying Cu layer from oxidation during thermal treatments.

The chemical structure and thermal stability of the mesoporous silica films were studied by Fourier transformation infrared spectroscopy (FTIR) (ASTeX PDS-17), thermal deposition mass spectroscopy (TDS) (TDS-APIMS, Hitachi Tokyo Electronics), and Auger electron spectroscopy (AES) (VG Microlab 310F). Transmission electron microscopy (TEM)(JEM-2010F) was used to study the microstructure of the film stack. Metal-insulator-semiconductor (MIS) capacitor structure was used for electrical measurements. An Al film with a thickness of 500 nm was evaporated on the back side of the Si wafer as the electrode. The Cu/Ta(N) electrode on the mesoporous silica layer has a mesa structure with the diameter of 0.2–0.8 mm. The dielectric constant and the leakage current density were measured by a Keithley model 590 CV meter and an HP 4156A semiconductor parameter analyzer, respectively. The bias-temperature stress (BTS) test was used to study mobile ion drift in the mesoporous films. During the BTS test, the capacitors were biased up to ± 20 V at 150 °C.

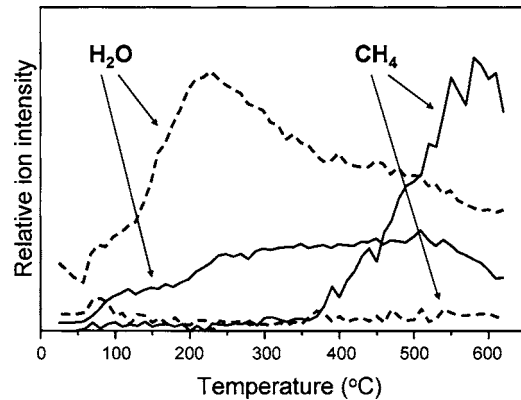


FIG. 1. Thermal desorption spectra of CH₄ ($m/e=16$) and H₂O ($m/e=18$) for the as-calcined (dashed line) and the HMDS-treated (solid line) mesoporous silica thin films.

III. RESULTS AND DISCUSSION

The as-calcined mesoporous silica thin film is inherently hydrophilic due to the presence of residual silanol terminal groups on the pore surface. Moisture uptake by these silanol groups can substantially degrade the dielectric property of the mesoporous silica thin film. In order to enhance hydrophobicity of the mesoporous dielectric layer, the as-calcined mesoporous silica thin film was trimethylsilylated before Cu-metallization by exposing the mesoporous film to HMDS vapor at 165 °C. The chemical stability of trimethylsilyl groups thereby introduced in the porous dielectric layer will have a great impact on the thermal and mechanical stabilities of the Cu-metallized film stack during subsequent high-temperature anneal treatments. The terminal trimethylsilyl groups might not be able to sustain their integrity after post-metallization thermal cycles. Hence, an understanding of thermal property of the surface terminal groups is of great importance for the implementation of mesoporous silica dielectrics in advanced copper interconnect technology.

A. Trimethylsilylation of the mesoporous silica thin film

Figure 1 shows thermal desorption spectra of H₂O and CH₄ for the as-calcined and the HMDS-treated mesoporous silica thin films. According to the TDS of H₂O ($m/e=18$, dashed line), a large amount of water evolved from the as-calcined mesoporous silica as the sample was thermally heated. Three desorption peaks can be clearly identified. The peak at the lowest desorption temperature (<80 °C) is due to physisorbed water, and the peak around 230 °C is likely due to weakly hydrogen-bonded water molecules.^{14,15} The peak at the highest desorption temperature is ascribed to the decomposition of silanol groups on the pore surface.^{14,15} After the HMDS vapor treatment water adsorption in the mesoporous silica thin film is greatly mitigated, as shown in the TDS of H₂O (solid line). The distinct intensity decrease of the OH-related desorption peak indicates that the HMDS treatment can effectively remove most silanol surface groups and this is supported as well by the FTIR study to be dis-

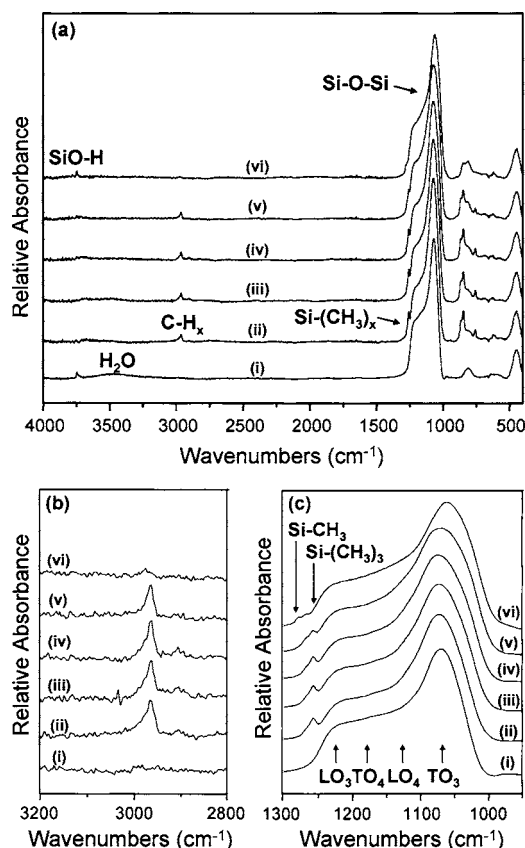


FIG. 2. (a) FTIR spectra of (i) the as-calcined film, (ii) the HMDS-treated film, and the HMDS treated film annealed at (iii) 300 °C, (iv) 400 °C, (v) 500 °C, and (vi) 600 °C. The enlarged absorption spectrum windows for the C–H stretching and the Si–O–Si asymmetric stretching modes are shown in (b) and (c), respectively.

cussed later. On the other hand, CH_4 ($m/e=16$, solid line) molecules, which can be ascribed to be an associative desorption product of methyl groups, began to desorb from the mesoporous silica thin film at ~ 375 °C, but significant desorption did not occur until the sample temperature exceeded 400 °C, and the desorption reached its maximum around 580 °C. This suggests that trimethylsilyl surface groups in the HMDS-treated mesoporous film are thermally stable up to 400 °C.

The FTIR study also indicated that notable decomposition of the trimethylsilyl surface groups took place at temperatures larger than 450 °C. Figure 2(a) shows FTIR spectra of the as-calcined, the HMDS-treated, and the annealed mesoporous silica thin films. Figures 2(b) and 2(c) are the enlarged absorption spectrum windows for the C–H stretching and Si–O–Si stretching modes, respectively. The as-calcined mesoporous silica films [Fig. 2(a)(i)] are rich in residual OH groups (~ 3600 cm^{-1}), and thus are liable to adsorb a large amount of water molecules (~ 3300 cm^{-1}). As shown in Fig. 2(a)(ii), an absorption peak developed at 1258 cm^{-1} , which is attributed to Si–CH₃ stretching vibration in the trimethylsilyl groups, and the methyl group-related C–H stretching peaks appeared around 2965 cm^{-1} after the HMDS vapor treatment, indicating that the mesoporous silica thin film was

effectively methylsilylated. In addition, the disappearance of the OH absorption peak and the broad water absorption band in the FTIR spectrum suggests that the mesoporous dielectric became hydrophobic after the HMDS treatment. When the HMDS-treated mesoporous silica film was thermally annealed, the intensities of the CH_x and the Si–CH₃ absorption peaks did not show discernable decrease until the annealing temperature was higher than 400 °C as revealed by Figs. 2(a)(iii) and 2(a)(v). The methylsilyl related absorption peaks shown in Figs. 2(b)(v) and 2(c)(v), which are for samples annealed at 500 °C, exhibit a slight intensity decrease, as compared with Figs. 2(b)(ii) and 2(c)(ii), implying that decomposition of trimethylsilyl terminal groups on the pore surface did take place at 500 °C, but the decomposition was rather moderate. On the other hand, the mesoporous silica annealed at 600 °C lost most of the intensity of the two CH₃ absorption peaks, and the Si–CH₃ peak had obvious changes in the peak's shape and position. According to Fig. 2(c)(vi), the peak at 1258 cm^{-1} for the sample annealed at 600 °C became vague, and two new absorption peaks emerged at 1268 cm^{-1} and 1278 cm^{-1} , which can be attributed to the Si–CH₃ stretching mode as well. It has been reported that a change in the number of the CH₃ moiety on the terminal Si–(CH₃)₃ group of the trimethylsilylated silica will cause slight shifts in the peak position of the Si–CH₃ stretching mode.^{16,17} The absorption peak centered at ~ 1278 cm^{-1} is attributed to the Si–CH₃ stretching of the monomethylsilyl group, and the absorption peak of the dimethylsilyl group is situated between the monomethylsilyl and trimethylsilyl peaks, around 1268 cm^{-1} . The obvious blueshift of the Si–CH₃ stretching absorption peak suggests that severe decomposition of terminal Si–(CH₃)₃ groups on the pore surface of the mesoporous silica thin film occurs at 600 °C. In addition, the significant intensity loss and dramatic change in the peak shape of the asymmetric CH₃–Si rocking mode, which is situated in the 700–900 cm^{-1} range,¹⁸ also indicates the decomposition of terminal Si–(CH₃)₃ groups at the high annealing temperature. In addition to the intensity variation of the absorption peaks associated with the Si–CH₃ group, the asymmetric Si–O–Si stretching absorption band situated between 1000 and 1300 cm^{-1} also reveals that the chemical structure of the silica matrix became less ordered as the annealing temperature increased. The asymmetric Si–O–Si stretching absorption band is, in general, assigned to be the overlap of two pairs of transverse optical (TO) and longitudinal optical (LO) modes.^{19–21} One of the two pairs denoted as TO₃–LO₃, is due to the asymmetric stretching motion of oxygen atoms moving in phase with neighboring oxygen atoms, and has the associated TO and LO peaks situated at ~ 1069 cm^{-1} and ~ 1223 cm^{-1} , respectively. The other pair, denoted as TO₄–LO₄, is due to the Si–O–Si vibration in which oxygen atoms execute stretching motion 180° out of phase with neighboring oxygen atoms, and has the TO₄ peak situated around 1177 cm^{-1} and the LO₄ peak around 1125 cm^{-1} . Previous studies suggested that the TO₄ and LO₄ modes in the SiO₂ matrix with a less ordered chemical structure have a greater absorption.^{20,21} By analyzing the intensity

TABLE I. Dielectric properties of the as-calcined and HMDS-treated mesoporous silica thin films after 400 °C anneal.

Film	Process conditions	k_{eff}	$J(\text{A}/\text{cm}^2)$ at 2 MV/cm
A	As calcined	>20	1.5×10^{-3}
B	HMDS treated	2.14	3.1×10^{-8}
C	Storage for 50 days	2.16	3.6×10^{-8}

variation of the absorption band of the Si–O–Si stretching modes, one can evaluate the microstructure ordering of the silica skeleton in the mesoporous silica thin film.¹² From Fig. 2(c), the Si–O–Si stretching absorption band of the HMDS-treated mesoporous silica has an almost identical peak position and shape as the as-calcined one, except the additional peak at 1258 cm^{-1} due to the Si–(CH₃)₃ stretching. This implied that trimethylsilylation by the HMDS treatment introduces little change in the chemical structure of the silica matrix of the mesoporous films. On the other hand, as shown in Figs. 2(c)(v) and 2(c)(vi), the LO₄ peak of the mesoporous film is apparently enhanced after the anneal at 500 °C, and a substantial change in the absorption shape of the Si–O–Si absorption band of the sample annealed at 600 °C. Combining previous discussion on the absorption peaks associated with the Si–(CH₃)₃ surface group, the chemical structure of the mesoporous silica thin film becomes less ordered upon the anneal at temperatures >450 °C due to the decomposition of terminal trimethylsilyl groups. The extensive decomposition of the trimethylsilyl surface group at 600 °C will have a destructive impact on the mechanical strength of the mesoporous silica thin films.

Table I lists the dielectric constant and the leakage current density of the HMDS-treated mesoporous silica film after annealed at 400 °C. For mesoporous silica films without the HMDS treatment, a rational capacitance-voltage (*C-V*) curve could not be obtained because the leakage current was enormously large. On the other hand, the mesoporous silica thin film receiving the HMDS treatment and 400 °C anneal has a dielectric constant as low as 2.14 and a leakage current density smaller than 3.1×10^{-8} A/cm² at 2 MV/cm. The significant decrease in the *k* value is ascribed to extensive elimination of water molecules physisorbed in the mesoporous silica film after the trimethylsilylation treatment. The trimethylsilylated mesoporous silica film is electrically reliable as shown by the dielectric property of the sample which was stored in cleanroom ambient for over 50 days. The trimethylsilylated mesoporous silica film shows little change in the dielectric constant and the leakage current density after the 50 shelf days, suggesting that bulky trimethylsilyl groups can effectively block further moisture uptake and, thus, the mesoporous silica thin film retains its hydrophobicity.

B. Thermal and chemical stability of the Cu/Ta(N)-metallized mesoporous silica film stack

When integrated into copper damascene process, the mesoporous silica dielectric faces many process challenges,

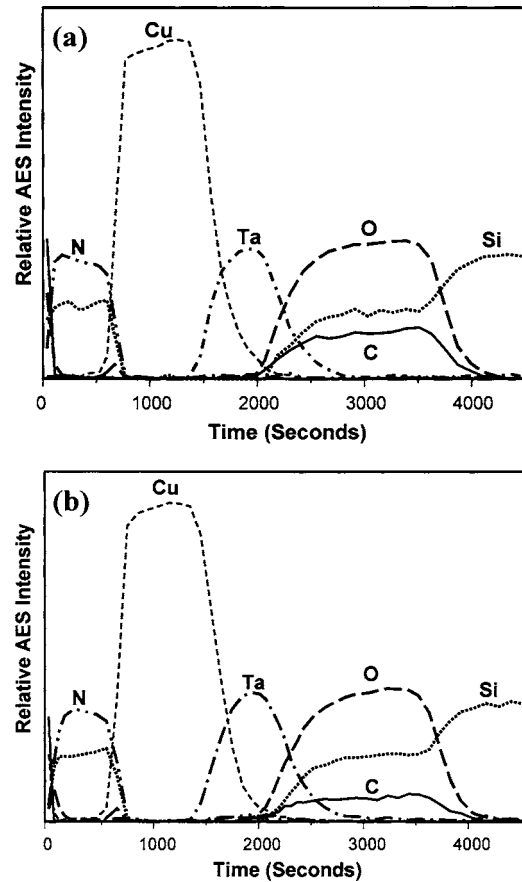


FIG. 3. AES depth profiles of the SiN_x/Cu/Ta(N)/mesoporousSiO₂/Si film stack after (a) 450 °C anneal and (b) 600 °C anneal.

such as solvent and gas penetrations via nanopores during cleaning, etch, and CVD processes. In particular, copper is a fast diffusing species in silicon dioxide and poorly adheres to most dielectric materials. This may become more severe when copper is bound to porous materials because a porous structure provides an effective path for surface diffusion and smaller contact area at the interface. Although a thin Ta or nitrided Ta [Ta(N)] barrier layer is always deposited between the Cu layer and the IMD layer to avoid Cu penetration, Cu can still diffuse into the IMD layer if any mechanical failure occurs to the barrier layer. Moreover, since trimethylsilylated mesoporous silica becomes chemically unstable at temperatures >500 °C as discussed before, the deposited Cu/Ta(N) layers may suffer film crack or interfacial failure as they are annealed at temperatures >500 °C. Therefore, thermal stability of the Cu/Ta(N) metallized mesoporous silica thin film is particularly critical to the success of the integration of mesoporous silica dielectric into the Cu damascene structure. In order to study the impact of thermal instability of the trimethylsilylated mesoporous silica layer to the integrity of the Cu interconnect structure, a film stack with an SiN_x(30 nm)/Cu(100 nm)/Ta(N)(30 nm)/mesoporous silica (200 nm)/Si layer structure was prepared and annealed at various temperatures. The nitride capping layer was deposited on the Cu layer to prevent copper from oxidation during anneals. Figure 3 shows Auger depth profiles for the film

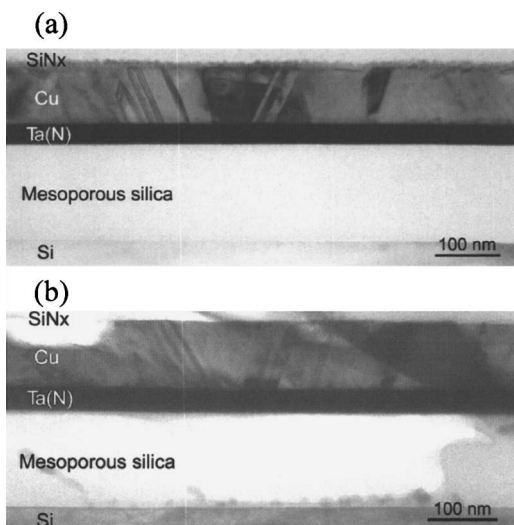


FIG. 4. Cross-sectional TEM images of the metallized film stack after (a) 450 °C anneal and (b) 600 °C anneal.

stack after thermal anneals at 450 °C and 600 °C. The AES depth profiles show that carbon distributes evenly in the mesoporous silica layer, implying that trimethylsilylation by HMDS treatment is uniform through the mesoporous silica layer. From the AES depth profiles, Ta(N) seems to be able to effectively prevent Cu from penetrating into the mesoporous silica layer. The tail of the Cu profile smoothly decaying into the mesoporous silica region is not due to copper diffusion, but is likely due to the ion mixing effect inevitably occurring during depth profiling. This will become clear when we discuss the BTS results later, which reveal no mobile ion drift in the mesoporous film. Compared with the sample annealed at 450 °C, the AES depth profile of film stack annealed at 600 °C shows a significant decrease in the carbon signal in the mesoporous silica layer. The heavy loss of the carbon content suggests that the decomposition of trimethylsilyl groups bounded on the pore surface is very severe at 600 °C.

Although TDS results indicate that the decomposition of trimethylsilyl groups on the pore surface becomes significant at temperatures >450 °C, the AES depth profiles shown in Fig. 3 seem not to reveal any discernible interfacial failure. Moreover, delamination at the interfaces in the metallized mesoporous silica film stack was not observed in scanning electron micrographs (not shown) even for the sample annealed at 600 °C, in which the mesoporous silica has suffered serious decomposition of trimethylsilyl groups on the pore surface. Figures 4(a) and 4(b) show the cross-sectional TEM micrographs of the metallized mesoporous film stack annealed at 450 °C and 600 °C, respectively. The TEM images clearly show that the interfaces between the neighboring layers in both samples are smooth and without separation. Since the decomposition of trimethylsilyl groups is severe at 600 °C as revealed by the FTIR, Auger depth profile, and TDS analysis, the undamaged interfaces may lead to an intuitive suggestion that the gaseous decomposition products either are small in quantity compared with the pore volume in the mesoporous silica layer, or can easily diffuse out of the

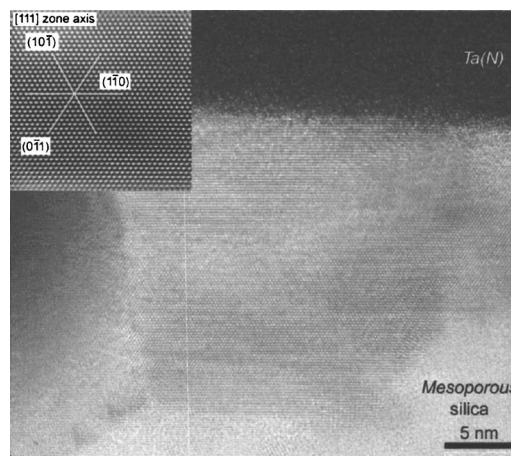


FIG. 5. HRTEM micrograph of the Ta₂C nanocrystal at the Ta(N)/mesoporous silica interface of the sample annealed at 600 °C for 30 min.

film stack through open pore channels in the porous layer. According to high-resolution TEM (HRTEM) study to be discussed, we found that decomposed alkyl species reacted with the Ta(N) barrier layer during the high-temperature anneal forming stable tantalum carbide at the interface between the barrier layer and the mesoporous silica layer. Figure 5 is an HRTEM image for the film stack annealed at 600 °C, and the image reveals the presence of a nanocrystal ~20 × 20 nm in size at the interface between the Ta(N) and the mesoporous silica layers. The nanosized phase was only found at sparse locations along the interface. The microstructure of this nanophase was analyzed in terms of fast Fourier transformation images. The lattice spacing of the nanocrystal viewed along the [111] zone axis was estimated to be 2.36 Å in the (10 $\bar{1}$) and (0 $\bar{1}$ 1) planes and 2.68 Å in the (1 $\bar{1}$ 0) plane. The angles between the (1 $\bar{1}$ 0) and (0 $\bar{1}$ 1) planes and between the (1 $\bar{1}$ 0) and (10 $\bar{1}$) planes were found to be 57.4° and 61.3°, respectively. The lattice parameters agree very well with the corresponding values for hexagonal Ta₂C structure (*p* $\bar{3}m1$).²² Combining the observations of the uniform decrease in the carbon content through the mesoporous silica layer and the undamaged interfaces strongly suggests that the Ta₂C nanocrystal was formed as a result of the reaction between the decomposed trimethylsilyl group and the Ta(N) barrier layer. It has been reported that gaseous species can diffuse through pore channels of nanoporous silica.^{23–25} As gaseous decomposed alkyl species suddenly evolve from the pore surface and diffuse through the porous silica layer to the interface, they can quickly react with Ta forming the stable carbide nanocrystal, thereby alleviating the tendency to mechanically damage the film stack during high-temperature anneals. Because of many desirable properties, such as excellent thermal stability, high melting temperature (3980 °C), high hardness (≥ 20 GPa), and chemical inertness, tantalum carbide has been proposed to be a potential diffusion barrier for Cu interconnect technology.²⁶ Although the presence of Ta₂C is a result of the decomposition of trimethylsilyl

groups, it does not cause apparent mechanical and electrical degradation in the metallized mesoporous silica film stack. Moreover, formation of the nanocrystal occurs at temperatures far above the typical process temperature of copper interconnect, and will not cause any integration difficulty for the trimethylsilylated mesoporous silica. The loss of the trimethylsilyl surface groups during annealing may change the effective dielectric constant of the film stack, we believe, however, the change is insignificant since these surface groups occupied only a small fraction of the pore volume.

Because AES has a relatively high detection limit, the Auger depth profiles shown in Fig. 3 cannot provide conclusive proof that Cu penetration into the mesoporous silica layer was completely retarded. In order to study if Cu ions diffused into the mesoporous silica layer after a typical interconnect annealing process at 400 °C, BTS measurement was carried out. The Cu-metallized mesoporous silica film stacks with and without the anneal treatment were biased at 20 V at 150 °C for 15 min so that Cu ions, if any, diffusing into the porous dielectric during the film stack process could be drifted to the dielectric/Si substrate or dielectric/gate electrode interfaces, depending on the bias polarity. The accumulated Cu ions would create uncompensated positive space charges at the interface. The positive space charges will result in a negative flat-band voltage shift in the $C-V$ curve at a positive gate bias and the magnitude of the voltage shift depends on the amount of charges. Because of the high porosity, the mesoporous silica dielectric has a much smaller cross-sectional area available for Cu diffusion than dense oxides, and the enormously large pore surface and the tortuous silica skeleton might lead to a complex Cu diffusion path under the vertical bias field in the film stack. This might lead to a smaller Cu diffusion rate in the porous dielectric than in dense oxide under the same BTS condition. Nevertheless, BTS measurement, combined with other characterization techniques, has been successfully used to study Cu ion diffusion in xerogel dielectric revealing that Cu ion diffusion was retarded in nanoporous silica.^{27–29} In the study, the BTS result of the unannealed sample shows little flat-band voltage shift under a constant positive or negative gate bias stress (± 20 V) as shown in Fig. 6(a). Figure 6(b) shows the BTS result for the film stack annealed at 400 °C, and little flat-band voltage shift was observed as well, suggesting that Cu diffusion into the trimethylsilylated mesoporous silica dielectric layer after the 400 °C anneal was negligible.

IV. CONCLUSIONS

In conclusion, thermal and electrical stability of a Cu/Ta(N)/mesoporous silica/Si film stack was studied. Hydrophobicity of the as-calcined mesoporous silica films spin coated on Si wafers was significantly improved by trimethylsilylation with HMDS vapor treatment. The presence of hydrophobic trimethylsilyl groups on the pore surface greatly enhances the resistance to moisture uptake, hence improving the dielectric property of the mesoporous film. According to FTIR, TDS, and AES studies, the trimethylsilylated mesoporous silica dielectric is thermally stable up to 400, and reli-

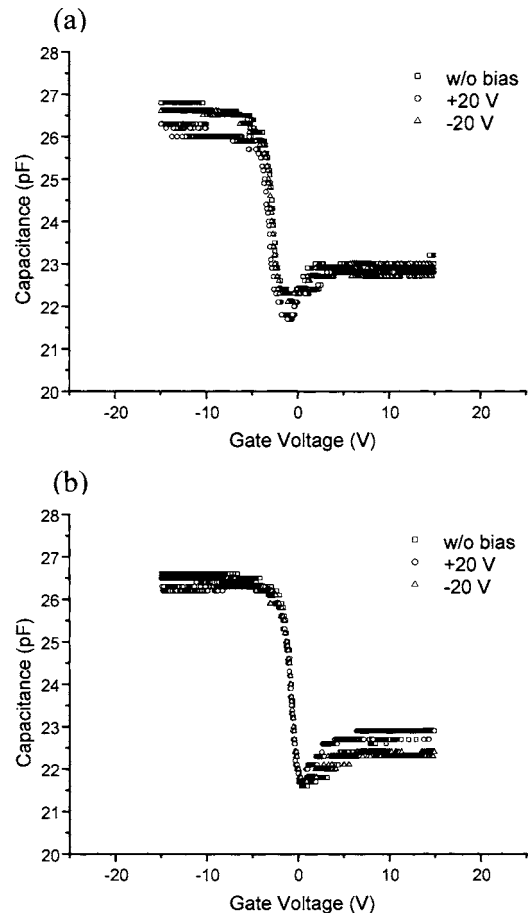


FIG. 6. $C-V$ traces of Cu-MIS capacitors stressed under various gate biases at 150 °C for 15 min: (a) Unannealed capacitor, and (b) capacitor annealed at 400 °C.

able over 50 days in terms of the dielectric and chemical properties. Decomposition of trimethylsilyl groups in the trimethylsilylated nanoporous silica thin film becomes obvious around 450 °C, and the mesoporous silica suffers serious degradation in chemical structure when the annealing temperature reaches 600 °C. However, decomposition-induced chemical degradation seemed not to cause any film crack and interfacial failure in the Cu-metallized mesoporous silica film stack, even for the sample annealed at 600 °C. HRTEM study reveals that a small number of Ta₂C nanocrystals were formed at the interface between the Ta(N) barrier layer and the mesoporous silica layer. The Ta₂C nanocrystal is suggested to be the reaction product of the decomposed alkyl species in the mesoporous silica layer and the Ta barrier layer during the high-temperature annealing process. The formation of the nanocrystal can relieve the tendency of possible film damage induced by the rapid evolution of gaseous decomposed species in the mesoporous silica layer. BTS measurements indicate that Cu diffusion into the mesoporous silica layer can be completely retarded in the Cu/Ta(N) metallized film stack annealed at 400 °C. The study shows that the trimethylsilylated mesoporous silica thin film is thermally and electrically stable up to 400 °C, and is a potential candidate as an ultralow- k dielectric for Cu damascene structure.

ACKNOWLEDGMENT

This work was supported by the National Science Council of the Republic of China under the Contract Nos. NSC93-2215-E-009-028 and NSC93-2120-M-009-007. Technical support from the National Nano Device Laboratories is gratefully acknowledged.

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