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Effects of H_2 Addition in Magnetized Inductively Coupled C_2F_6 Plasma Etching of Silica Aerogel Film

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Effect of H_2 addition to C_2F_6 plasma etching of SiO_2 aerogel film was examined for low-k dielectric application. In this experiment, H_2 plasma in itself was responsible for pore blocking and bond breaking of the SiO_2 aerogel. With increasing hydrogen from 0 to 50%, etch rate of SiO_2 aerogel was severely dropped at 20% of H_2 addition. According to the increase in H_2 addition, transition from fluorine-rich residue to carbon-rich one was gradually happened in SiO_2 aerogel. Surface microstructure of SiO_2 aerogel was so influenced with the increasing H_2 addition that they transformed to be planar by the interaction between residue/network and ion bombardment and the condensation reaction of surface chemicals with H_2 plasma.

KEYWORDS: SiO_2 aerogel, plasma, etching, H_2, C_2F_6, low-k dielectric, residue

1. Introduction

In future integrated circuit chip technology the accomplishment depends critically upon the development of new dielectric insulators with dielectric constant substantially lower than what achieved to date.[1)] Low k materials lower line-to-line capacitance, reduce cross-talk noise in interconnect structure, and alleviate power dissipation issues. Various silica films, such as fluorinated silica, organic silica, and porous silica are promising for low dielectric materials. Especially, porous silica, depending on the porosity, can give a dielectric constant below 2.[2,3)] However, for the application of these materials (dielectric constant close to or below 2), there are lots of things established.

As one of manufacture processes, etching behavior must be fully understood because of its porous structure. In this work, we investigated the role of H_2 gas in fluorocarbon C_2F_6 plasma etching. The selective etching of SiO_2 over underlayer materials employing fluorocarbon plasma is a very important technology in the fabrication of ultra large-scale integrated (ULSI) circuits. As minimum feature size of devices decreases to 0.1 μm regime in ULSI, high-density plasma sources at low-pressure operation such as inductively coupled plasma (ICP) have been proposed because they can achieve highly anisotropic etching with high etch rate.[4)] Recently, H_2 plasma treatment containing very intense vacuum ultraviolet (VUV) emissions has been used for the photochemical treatment of surface organic and hydroxyl. The role of VUV in the plasma is an initiation reaction like atomic oxygen particle (ion).[5)]

Low pressure plasma treatment is increasingly used as an effective method for surface modification. Low pressure plasmas consist of a complex mixture of charged particles (electron, ions) and neutrals. They can also be efficient sources of electromagnetic radiation; the radiation in VUV, $\lambda < 200$ nm corresponds to photon energies at least twice the covalent bond strength of most molecules, and it plays a vital role in the initiation of photochemical processes, both at sample surface and in gas phase.[6)]

In this work, we investigated the effects of H_2 addition to C_2F_6 plasma etching of SiO_2 aerogel film comparative to thermal SiO_2 on the etch rate, surface morphology, and surface compositions/bonding states.

2. Experimental Procedures

SiO_2 aerogel films were fabricated by spin-coating and supercritical drying method on p-doped Si (100) wafers.[2)] The films were 11,000–12,000 Å thick with porosity of 65–70%. The porosity was determined by obtaining areal density using Rutherford backscattering spectrometry (RBS) technique and the thickness was measured using nanospec and scanning electron microscopy (SEM, Hitachi, S4200). Plasma treatments and etching experiments of SiO_2 aerogel and thermal SiO_2 were conducted in a planar magnetized inductively coupled plasma (MICP) reactor for 30 s. The chamber was evacuated until 1×10^{-6} Torr and the processing gas was introduced. C_2F_6+H_2 (0, 10–50%) and H_2 (100%) gases were used. In this experiment, inductive power was 400 W and bias voltage was -100 V at 13.56 MHz of RF. The bias voltage was controlled as 0 V by applying rf bias power. The total pressure was maintained at 5 mTorr. Surface morphology was observed using SEM. The chemical composition and bonding state of partially etched SiO_2 surface were investigated using X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 220i-XL).

3. Results and Discussion

For verifying intrinsic H_2 plasma effect, we performed H_2 plasma treatment of SiO_2 aerogel at first. Figure 1 shows surface micrographs of SiO_2 aerogel treated for 30 s without and with bias of -100 V. There showed closure of pores and planarization of surface (Figs. 1(b) and 1(c)). Thickness decreased to the degrees of 10 and 17%, respectively and more densified surface microstructure was obtained with applying bias voltage. This is ascribed to the increase of bias rf power, VUV intensity, and the acceleration energy of reactive ions. Only two-member ring structure gives an exothermic addition of H_2 to Si-O bonds with the formation of Si-H and O-H groups.[5)] In case of high density H_2 plasma treatment, interactions between H_2, H^+, H_2^+, H^*, H_2^*, etc and point defects of silica, in particular dangling bonds, and between vacuum ultraviolet (VUV) of 121.5 nm Lyman a line and C-H, C-O, C-C bonds have to be considered.

XPS analysis was performed to study the bonding states of transformed surface and given in Fig. 2. Si 2p photoelectron spectrum was only changed in with -100 V of bias, i.e. dam-

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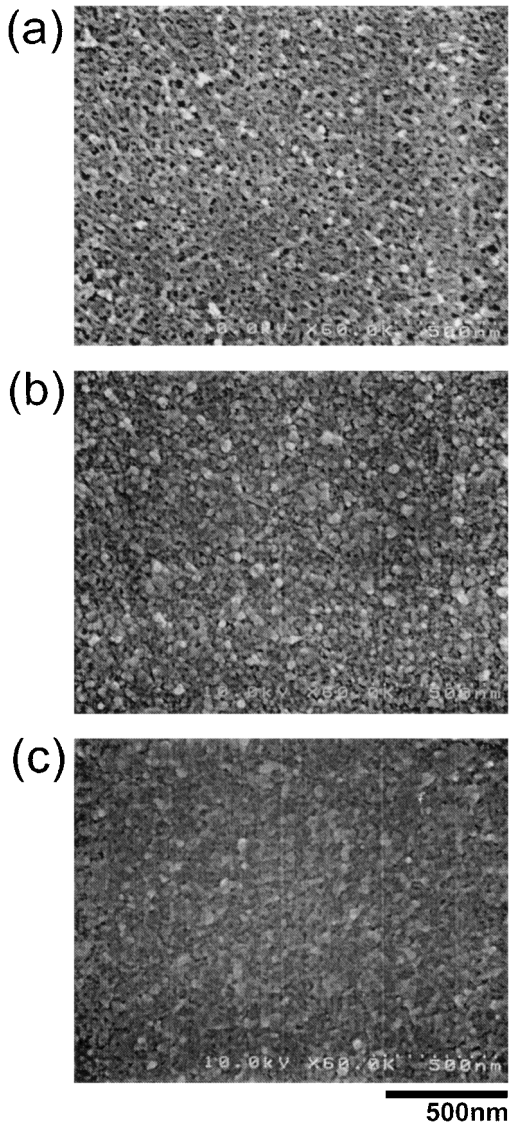

Fig. 1. SEM micrographs (a) before and after H_2 plasma treatment of SiO_2 aerogel at 400 W of rf power, 5 mTorr of pressure, and (b) 0 and (c) −100 V of bias voltages.

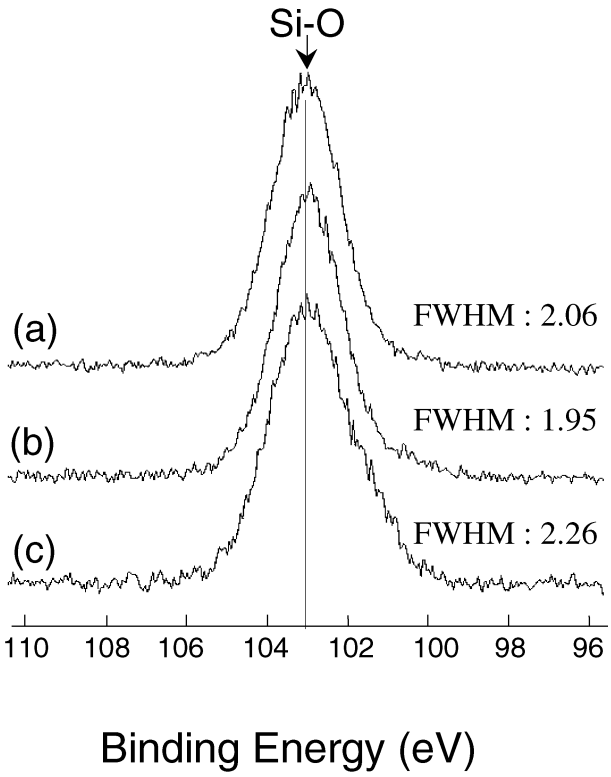

Fig. 2. XPS Si 2*p* peak (a) before and after H_2 plasma treatment of SiO_2 aerogel at 400 W of rf power, 5 mTorr of pressure, and (b) 0 and (c) −100 V of bias voltages.

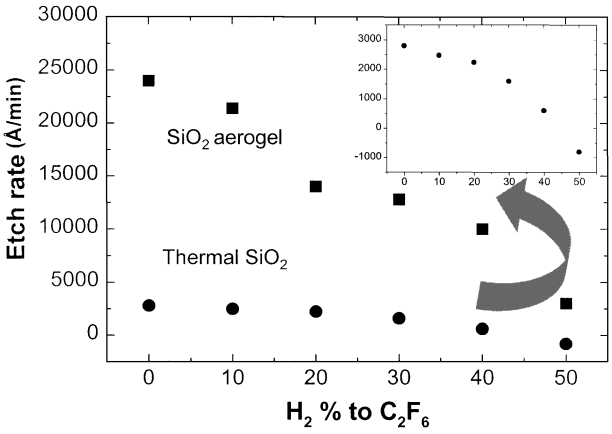

Fig. 3. Dependence of H_2 addition to C_2F_6 on the etch rate of SiO_2 aerogel and thermal SiO_2: etching at 400 W of rf power, 5 mTorr of pressure, and −100 V of bias voltage.

aged and partially reduced Si-O bonds. The sample treated without bias showed that the surface state was easily recovered after exposure to air for transferring to XPS analysis. However the sample treated with −100 V of bias showed that surface state was not recovered due to the ion bombardment with high energy and large penetration depth.

In order to investigate the effect of hydrogen addition (0–50%) on the etching of SiO_2 aerogel and thermal SiO_2, their etch rates are monitored and given in Fig. 3. RF inductive power, bias voltage, and process pressure were 400 W, −100 V, and 5 mTorr, respectively. C_2F_6 gas is highly polymerizing and the addition of small amounts of hydrogen reduces the concentration of free fluorine by forming HF. This fluorine deficient discharge is important since it enables selective etching.[6] The etch rate of SiO_2 aerogel film was observed 6–8 times higher than that of thermal SiO_2. Even though the porosity of SiO_2 aerogel (65–70%) is considered, the relative etch rate of SiO_2 aerogel is still higher than that of thermal SiO_2, because SiO_2 aerogel provides large surface area.[2,3,7] As can be seen in Fig. 3, with increasing hydrogen from 0 to 50%, etch rate of SiO_2 aerogel was severely dropped at 20% of H_2 addition, whereas thermal SiO_2 above 30%. With SiO_2 aerogel, it can be ascribed to the carbon- and hydrogen-rich surface chemicals [–OH, –OR; R = C_2H_5]. Hydrogen limits its etch rate by inducing free fluorine deficiency and leads to suppressive deposition period. Carbon also lowers etch rate by forming a polymer residue film. With thermal SiO_2, the decrease in etch rate according to the addition of hydrogen mainly depends on the induction of free fluorine deficiency.

The typical RBS spectra obtained from the before and after etching of SiO_2 aerogel films for 30 s with C_2F_6 plasma are shown in Fig. 4. The peak area is concerned with two factors; the amount of atoms in film and the thickness of film. By comparing the peak area of the constituent atoms in the

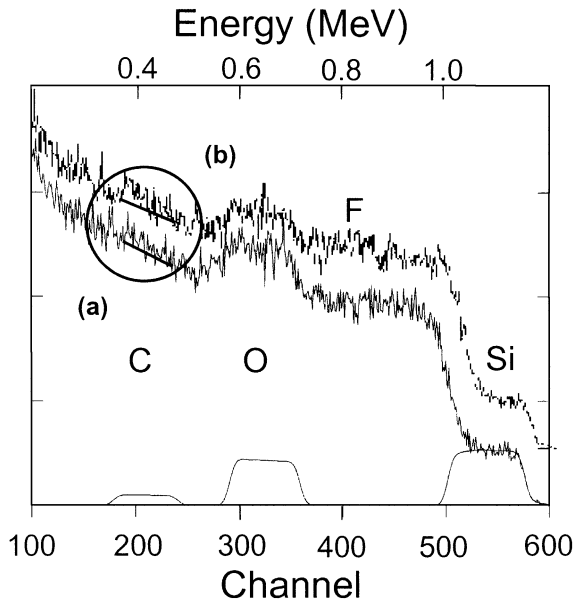

Fig. 4. RBS spectra of (a) before and (b) after partial etching of SiO_2 aerogel film with C_2F_6: etching at 400 W of rf power, 5 mTorr of pressure, and −100 V of bias voltage.

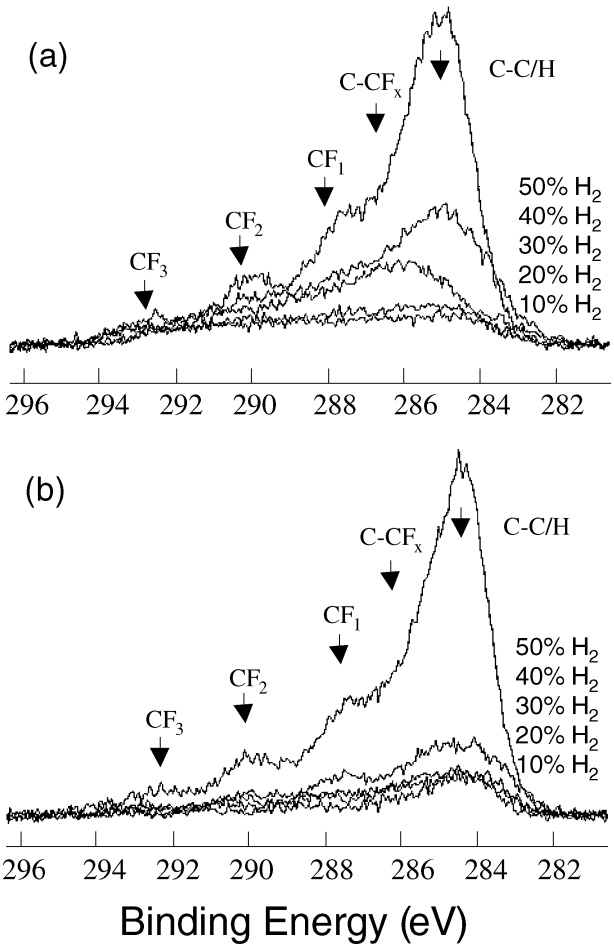

Fig. 5. XPS C 1*s* peak shape changes in partially etched (a) SiO_2 aerogel and (b) thermal SiO_2 films according to various H_2 contents in C_2F_6 plasma; etching at 400 W of rf power, 5 mTorr of pressure, and −100 V of bias voltage.

spectra, the atomic ratios of Si:O:C:F were measured to be 1:2.3:0.9:0 and 1:2.3:1:0.5 for the before and after etching of the films, respectively. The increase of relative atomic ratio of carbon after etching reflects the formation of fluorocarbon polymer residue.

Figure 5 shows C 1 s photoelectron peaks in the XPS spectra of partially etched SiO_2 aerogel and thermal SiO_2 films. The bonding states of carbon showed the formation of fluorocarbon residue film on the partially etched oxide films. The increase in absolute intensity according to hydrogen addition agreed well with the decrease in etch rate as shown in Fig. 3. Especially in both cases, the relative intensities of C-C/H related bonds (C-CF_x and C-C/H) increased while those of C-F related bonds (–CF_3, –CF_2, and –CF_1) decreased with increasing hydrogen content. This seemed due to the hydrogen reduction of fluorocarbon polymer residue because hydrogen formed volatile HF with fluorine of the residue film.

The surface compositional changes of SiO_2 aerogel and thermal SiO_2 films with various hydrogen contents in C_2F_6 plasma is obtained using XPS and given in Fig. 6. The increasing behavior of C and F of the films agreed well with the decrease in the etch rate. Relatively higher contents of F and C were observed in SiO_2 aerogel than thermal SiO_2. This was due to the large amount of residue formed on the surface of partially etched SiO_2 aerogel by surface chemicals and structural effect, i.e. there was a shadowed zone in SiO_2 aerogel film, under-hemisphere surface of networking particles, where ion bombardment on fluorocarbon residue was rarely happened.[7–9] Even though SiO_2 aerogel film contained carbon atoms as surface organic group, its F/C ratio was higher than thermal SiO_2 and this agreed well with the evolution of bonding states in C 1*s* spectra of the films (Fig. 5). It could be also understood from the porous microstructural characteris-

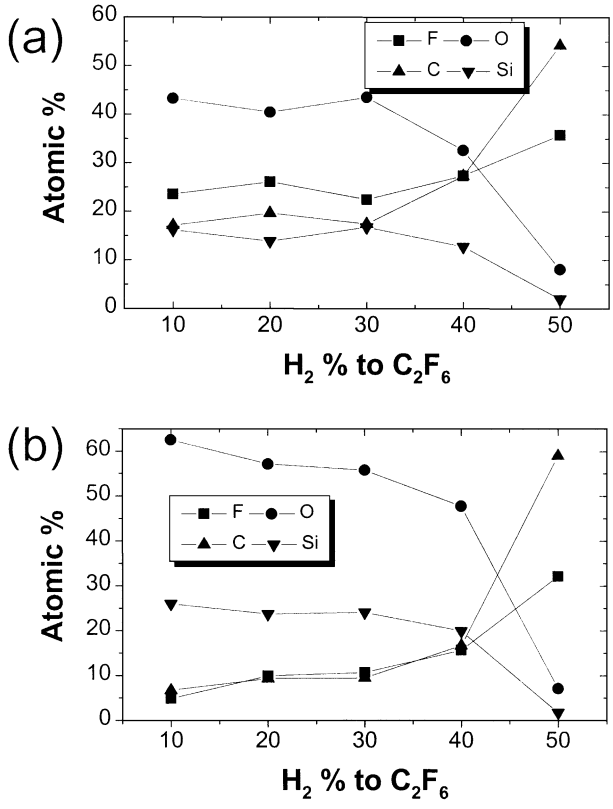

Fig. 6. Compositional changes of (a) SiO_2 aerogel and (b) thermal SiO_2 films according to various H_2 contents in C_2F_6 plasma; etching at 400 W of rf power, 5 mTorr of pressure, and −100 V of bias voltage.

tic of SiO_2 aerogel film.

Microstructures of surface after partially etched SiO_2 aerogel films were dramatically changed with H_2 addition to C_2F_6 by ion bombardment and/or competitive etching/deposition reaction. Figure 7 shows that the images of surface microstructure changed gradually in the sequence of abrupt etching (b), surface blocking (c), and planarized surface network (d) with increasing hydrogen content. It could be also considered from the ion energy and VUV effect of H_2 plasma seen in Figs. 1 and 2. Ion bombardment energy was absorbed and distributed to particle and branch in the alleviation of fluorocarbon residue and SiO_2 network structure. Then, the agglomeration of particles and network was come from at the cost of condensation of the surface organic and hydroxyl with energetic H_2 plasma. Physical effects by ions must be diminished by the presence of thick residue layer (coated on skeleton) and SiO_2 skeleton (neutralization of ion). Moreover, broken off-clusters of fluorocarbon residue on the silica network by ion bombardment were deposited on the inner space. The residue layer and surface chemicals trapped fluorine atoms, preventing the etchant from transport into the film, and absorbing the bombarding energy of ions.

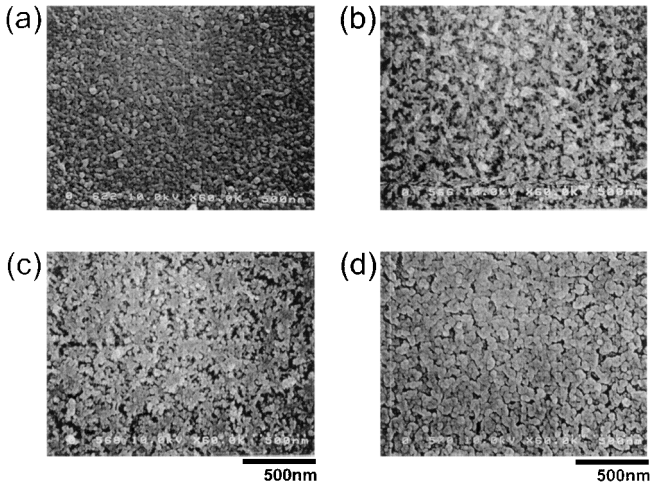

Fig. 7. SEM micrographs of (a) before and partially etched SiO_2 aerogel films with (b) 10, (c) 30, and (d) 50% of hydrogen containing C_2F_6 plasma; etching at 400 W of rf power, 5 mTorr of pressure, and -100 V of bias voltage.

4. Conclusions

The etching behavior of SiO_2 aerogel films were studied using H_2 and C_2F_6/H_2 plasmas in comparison to thermal SiO_2. Closure of surface pores and planarization of surface were observed on SiO_2 aerogel film after etching, effectively with applying bias and increasing hydrogen content in plasma gas. Fluorine-rich fluorocarbon polymer residue turned to be carbon-rich one according to hydrogen content and etch rate decreased in both oxide films. Hydrogen in plasma seemed to limit etch rate by inducing free fluorine deficiency and lead to suppressive deposition process. Due to the microstructural characteristic of SiO_2 aerogel film, porous with networking particles, relative atomic ratio of F and C was found to be higher than thermal SiO_2 after partial etching, i.e. larger content of fluorocarbon polymer residue. Furthermore F/C ratio in the residue film of SiO_2 aerogel was also higher than thermal SiO_2.

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1) N. Forgotson, V. Khemka and J. Hopwood: J. Vac. Sci. Technol. **B14** (1996) 732.
2) M. H. Jo and H. H. Park: Appl. Phys. Lett. **72** (1998) 1391.
3) C. J. Brinker and G. W. Scherer: *Sol-Gel Science* (Academic Press, San Diego, 1990) Ch. 14, p. 859.
4) J. Fricke and A. Emmerling: J. Am. Ceram. Soc. **75** (1992) 2027.
5) Z. H. Liu and N. M. D. Brown: J. Phys. D: Appl. Phys. **31** (1998) 1771.
6) M. H. Jo, H. H. Park, D. J. Kim, S. H. Hyun, S. Y. Choi and J. T. Paik: J. Appl. Phys. **82** (1997) 1299.
7) C. J. Brinker and G. W. Scherer: *Sol-Gel Science* (Academic Press, San Diego, 1990) Ch. 9, p. 557.
8) S. J. Wang, I. S. Jin and H. H. Park: Surf. Coat. Technol. **100-101** (1998) 59.
9) S. J. Wang, H. H. Park, S. H. Hyun and G. Y. Yeom: to be published in Appl. Surf. Sci.