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Applied Surface Science 169–170 (2001) 457–462

applied surface science

www.elsevier.nl/locate/apsusc

The effects of surface terminal bonds and microstructure of SiO_2 aerogel films on dry etching

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Received 2 August 1999; accepted 5 November 1999

Abstract

The effects of microstructure and surface terminal bonds of SiO_2 aerogel films on dry etching were investigated using Ar, SF_6, and C_2F_6 plasma gases. With Ar plasma etching, physical effect of ion bombardment on porous film was found. In residue-free SF_6 plasma etching, reactive etchant transport and high-mass ion bombardment were observed. With C_2F_6 plasma etching, fluorocarbon residue layer was revealed to maintain surface morphology as acting a barrier to radical transport and ion bombardment. An etching of 450°C-annealed SiO_2 aerogel showed that a dense surface induced the decrease in reaction area, inhibition of etchant transport, and then uniform etching.

Keywords: Low dielectric; SiO_2 aerogel; Plasma etching; Surface chemicals; Porous structure

1. Introduction

As critical dimensions continue to decrease in the submicron regime, the once minimal interconnection delay becomes a prime concern. One method for reducing interconnection delay is to replace conventional SiO_2 with lower dielectric constant (low-k) material ($k < 3$). SiO_2 aerogel can also be a strong candidate for conventional intermetal dielectric (IMD) materials [1]. In our previous study, we obtained a SiO_2 aerogel film with dielectric constant of 2.1 at 1 MHz through spin-coating and super critical drying method [2,3]. However, this fabrication technique induces high porosity (large surface area) and terminal groups (–OH, –OR, etc.) [1–4]. In order to use SiO_2 aerogel films as an IMD material, a study of etching behavior is indispensable for application level. Porosity and surface chemical effects on the etching process must be considered in the various points of view. In this study, the etching behavior of SiO_2 aerogel films was investigated with respect to porous structure and surface terminal bonds.

2. Experimental

SiO_2 aerogel films were fabricated by spin-coating and supercritical drying method on p-doped Si (1 0 0) wafers. Specific details of the film preparation were given in elsewhere [2,3]. The SiO_2 aerogel films were 11,000–12,000 Å thick. To obtain specimens free from C and H, they were annealed at 450°C for 2 h in an air-atmosphere. Etching experiments were conducted in a planar magnetized inductively coupled

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0169-4332/01/$ – see front matter
PII: S0169-4332(00)00703-0

plasma (MICP) reactor. Argon, SF_6, and C_2F_6 gases were used as etching gases. In this experiment, an inductive power was 400 W and a bias voltage was −100 V at 13.56 MHz of RF power. A total pressure was 5 mTorr. Etching time was 1 min in argon plasma or 30 s in SF_6 and C_2F_6 plasma. The chemical composition of partially etched SiO_2 surface was evaluated using X-ray photoelectron spectroscopy (XPS). The analyses were performed with a VG Scientific ESCALAB 220*i*-XL spectrometer, and the photoelectrons were excited using Kα of Mg (1253.6 eV) irradiation operated at 250 W. Etched samples were preserved in N_2 atmosphere before the measurements. Surface morphology was observed using scanning electron microscope (SEM, Hitachi, S4200).

3. Results and discussion

SiO_2 aerogel films have a large surface area. Main concerns were laid in the inherent nature of porous structure and surface terminal bonds of the film. Surface terminal bonds consist of hydroxyl (–OH) and organic (–OR; $–OC_2H_5$) groups [1,2,4]. Hydrogen atoms are terminal.

Fig. 1 shows the surface morphologies before and after 450°C-annealing of the SiO_2 aerogel film. A great number of –OH and –OR groups were eliminated by condensation reaction [4,5]. Particle-size increased and pore-size decreased after the annealing. By thermal condensation, thickness shrunk from 12,000 to 7500–7700 Å, measured porosity decreased from 70 to 45% by Ellipsometer [2].

Non-reactive Ar plasma etching was performed to investigate the physical effects on the porous structure. In Fig. 2, surface morphologies after partial Ar plasma etching are shown. Argon rf plasma processing is a non-selective and purely physical impact-based process. Argon plasma brings about the decomposition of bonds, sputtering of film constituents, surface reorganization and re-deposition of sputtered atoms and clusters [6]. In case of non-annealed SiO_2 aerogel

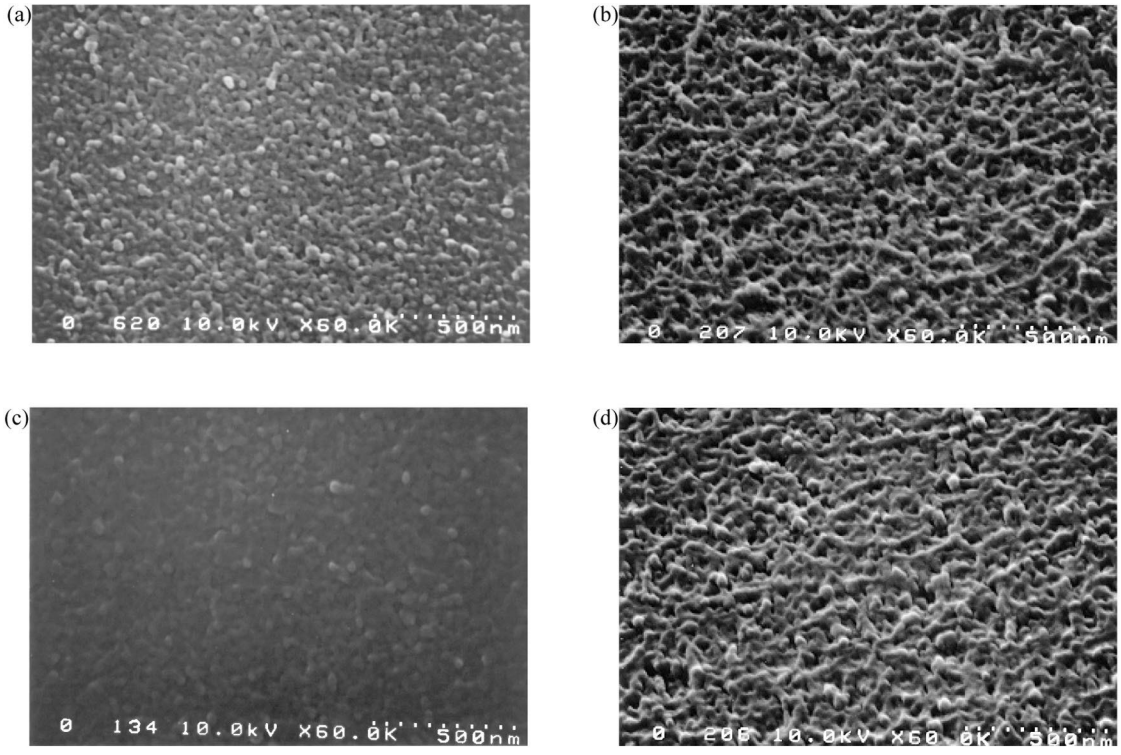

Fig. 1. Planar SEM images of SiO_2 aerogel films: (a) non-annealed; (b) 45° tilted image of (a); (c) annealed at 450°C and (d) 45° tilted image of (c).

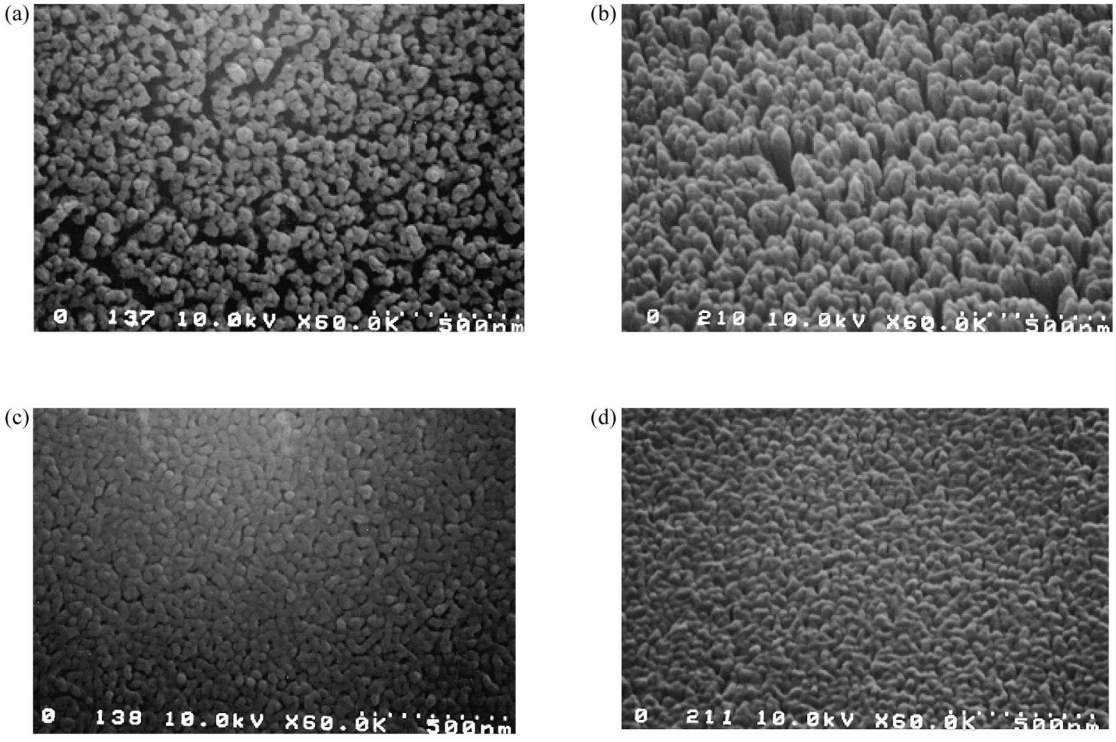

Fig. 2. Planar SEM images SiO_2 aerogel films after partial Ar plasma etching: (a) non-annealed; (b) 45° tilted image of (a); (c) annealed at 450°C and (d) 45° tilted image of (c).

film, Fig. 2(a) and (b), the effects of Ar^+ ion bombardment are shown as network destruction, particle coarsening, and formation of pillar-like structure. High energy-vacuum ultraviolet (VUV) radiation by metastable Ar^* ($Ar^* \rightarrow Ar + h\nu$) can be also the cause of particle coarsening from the scission of O–H, O–C, C–C, and C–H bonds [7]. Same process was done to 450°C-annealed film. After the etching, surface was revealed to be somewhat flat exhibiting a good interconnection of particles. It is due to a planar and condensed morphology of annealed film, i.e. two-dimensional structure as thermal SiO_2. So, it could be said that dense surface could endure the destruction of interconnected network structure by Ar^+ ion bombardment.

By using SF_6 plasma, the etching behavior of porous SiO_2 film without a formation of fluorocarbon polymeric residue could be studied. Fig. 3 shows very different etched surface morphologies between non-annealed and 450°C-annealed films. With the non-annealed sample, reactive etchant could move into the film and react with Si–O network from all directions easily, because there are many pores and no barrier against the etching reaction like a fluorocarbon residue. Angle-resolved XPS analysis allowed us to reveal a three-dimensional etching behavior of SiO_2 aerogel film with CHF_3 gas in our previous study [8]. On the contrary, with the 450°C-annealed sample, surface morphology was uniform to some extents as shown in Fig. 3(c) and (d). Because the pore size of the annealed film was smaller than that of the non-annealed film, probability of etching gas-transport diminished and inside-etching of the film hardly proceeded. As a result, it could be said that porous films permitted a large transport of etching species and an abrupt inside-etching of the film. A bombardment by incident SF_x^+ ions (SF_5^+, SF_4^+, etc.) with high mass could induce a rougher surface than a bombardment by Ar^+.

Fig. 4 shows surface morphologies after C_2F_6 plasma etching of SiO_2 aerogel films. The surface morphologies of the C_2F_6 plasma etched films were

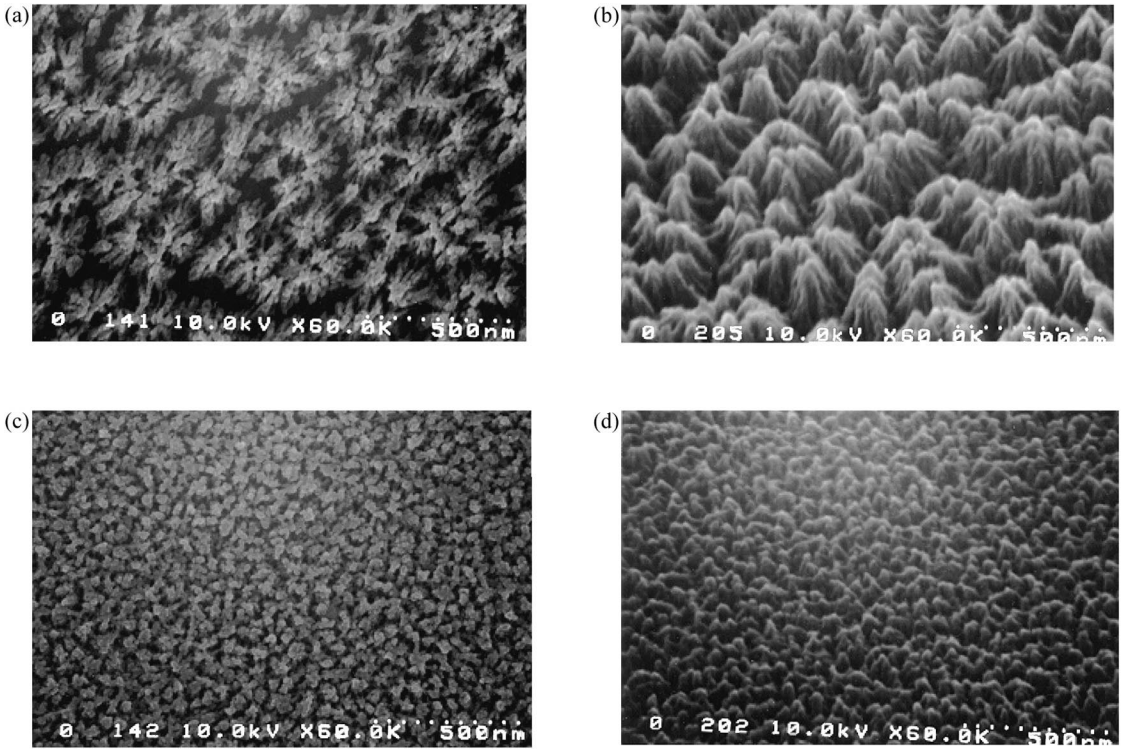

Fig. 3. Planar SEM images of SiO_2 aerogel films after partial SF_6 plasma etching: (a) non-annealed; (b) 45° tilted image of (a); (c) annealed at 450°C and (d) 45° tilted image of (c).

smoother than those of the SF_6 plasma etched films. However particle size and shape were similar with those of SF_6 plasma etching. In C_2F_6 plasma etching, a fluorocarbon residue could be easily formed and etching did not proceed heavily as SF_6 plasma etching. The residue layer trapped the fluorine atoms, preventing the etchant from transport into the film, and absorbing the bombarding energy of CF_x^+ ions. Consequently, it could be said that etched surface morphology mainly depends on the porosity of films.

As shown in Fig. 5, XPS reveals a substantial difference in O/Si ratio after various plasma etching. Higher ratio than 2 is a characteristic of large surface area of porous film. The O/Si ratio is almost same in non-annealed and 450°C-annealed samples. After Ar plasma etching, O/Si ratio was lower in the non-annealed film. In the non-annealed film, atoms and clusters could be easily sputtered through the pores by incident Ar^+ ion. While, in the annealed film, small pore size due to particle agglomeration might result in the decrease of sputtering probability. In SF_6 and C_2F_6 plasma etching, chemical reaction should be considered for the variation of O/Si ratio. In spite of dense microstructure of the annealed films, smaller ratio of O/Si is obtained than the non-annealed samples. That is, in non-annealed films, surface terminal hydrogen atoms inhibited the detachment of oxygen from Si–O network by the HF formation. In C_2F_6 plasma etching, this effect is intensified due to the formation of residue layer.

4. Conclusion

Non-annealed and 450°C-annealed SiO_2 aerogel films were etched using Ar, SF_6, and C_2F_6 plasma gases. Argon plasma etching, characterizing a non-selective and physical impact based process, induced network destruction, particle coarsening, and formation of pillar-like structure. The effects of high mass ion bombardment and reactive etching species could be analyzed in the etching of SF_6 gas. With

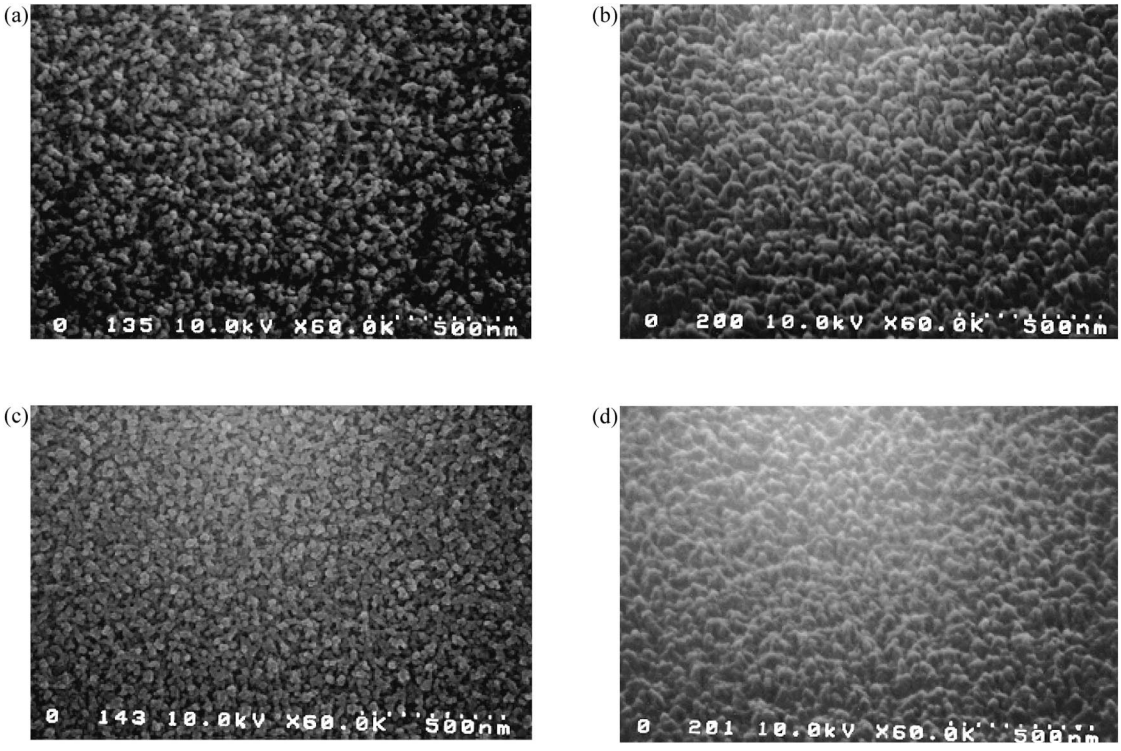

Fig. 4. Planar SEM images of SiO_2 aerogel films after partial C_2F_6 plasma etching: (a) non-annealed; (b) 45° tilted image of (a); (c) annealed at 450°C and (d) 45° tilted image of (c).

the non-annealed sample, inside-etching of porous film was observed, i.e. three-dimensional etching of the film. In C_2F_6 plasma etching, fluorocarbon residue layer played roles of trapping the fluorine atoms, preventing the etching species from transport into the film, and absorbing the bombarding energy of CF_x^+ ions. Etching of the annealed films showed that surface morphology was greatly influenced by the porous nature of film.

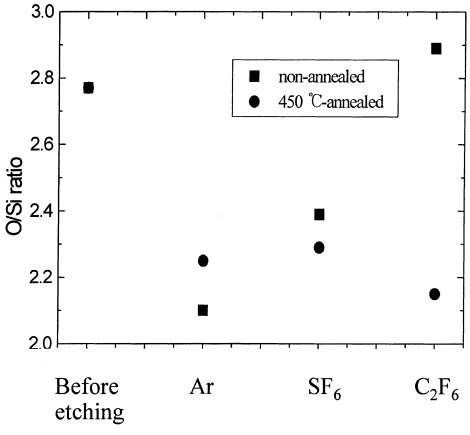

Fig. 5. Surface O/Si ratios of non-annealed and 450°C-annealed SiO_2 aerogel films before and after etching with Ar, SF_6, and C_2F_6 gases.

Acknowledgements

The authors of this paper would like to thank the Samsung Electronics Company for its support of this research.

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