

A Preliminary Study on the Etching Behavior of SiO₂ Aerogel Film with CHF₃ Gas

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Etching behavior of SiO₂ aerogel film has been investigated in order to examine the feasibility of its application to an interlevel dielectric material. Low dielectric property of SiO₂ aerogel film is simply originated from its highly porous structure, but interconnected particles are covered with surface chemical bondings (-OH, -OC₂H₅, *etc.*). Etching experiments have been performed with high density inductively coupled CHF₃ plasma. The effects of porous structure and surface chemical bondings on the etching of SiO₂ aerogel film have been analyzed. The changes of surface morphology were observed using scanning electron microscopy. X-ray photoelectron spectroscopic analyses revealed compositions and chemical bonding states of reaction layer. From the analyses, 3-dimensional etching was not feasible macroscopically in SiO₂ aerogel film even with its porous nature because network structure was maintained through the etching process. Internal surface chemicals seemed to act as an etching barrier by reacting with active fluorine and to control the etch rate.

I. INTRODUCTION

The growth of integrated circuits (IC) technology is primarily based on the continued scaling down of devices to the smallest dimension. Smaller devices give higher packing density as well as higher operating speed. In ultra large scaled integration (ULSI) era, low dielectric material is indispensable for fulfilling the desired functions in order to operate. Sol-gel derived SiO₂ aerogel film with nano-scaled particles and pores easily shows low dielectric constant (2.0~2.5) by its structural characteristic [1]. The basic properties of the SiO₂ aerogel film have been reported in several articles [1,2].

The real challenge in using this low dielectric material for interlayer dielectric (ILD) applications will be in its compatibility with standard device fabrication process. Many different processing issues such as film adhesion, compatibility to various chemicals, etching of via holes, photoresist stripping, *etc.*, must be carefully studied. Although many researches have contributed in the formation and characterization of SiO₂ aerogel films, there have been little work done on the etching of SiO₂ aerogel due to its distinguishable porous nature from thermally grown SiO₂. Its porous structure and surface chemicals composed of large amounts of carbon and hydrogen are due to the characteristic of sol-gel process. The main

content of this work is to reveal the preliminary etching behavior of SiO₂ aerogel film compared with thermally grown SiO₂ film as a reference and to study the feasibility of using the film for low dielectric interlayer film in ULSI multilevel interconnection.

II. EXPERIMENTAL

SiO₂ aerogel films were fabricated by sol-gel method and spin-coating on Si substrate. Specific details of SiO₂ aerogel film preparation are given elsewhere [1,3]. The etching of SiO₂ aerogel films was performed together with thermally grown SiO₂ film for comparison. High density inductively coupled plasma (ICP) equipment was used for the etching experiment. The etching gas was CHF₃. The rf inductive power was 400 W and the bias voltage was -100 V at 13.56 MHz of rf power, and the process chamber pressure was 10 mTorr.

The porosity of SiO₂ aerogel film was measured by Rutherford backscattering spectrometry. The surface morphology of the samples was observed by scanning electron microscopy (SEM). The etch rate of SiO₂ aerogel film was taken from cross-sectional SEM images and for thermally grown SiO₂ film, α -step and Nanospec were used. Partial or over-etched sample surfaces were studied using x-ray photoelectron spectroscopy (XPS). The photoelectrons were excited using standard Mg K α (1253.6 eV) radiation operated at 250 W. Narrow scan spectra

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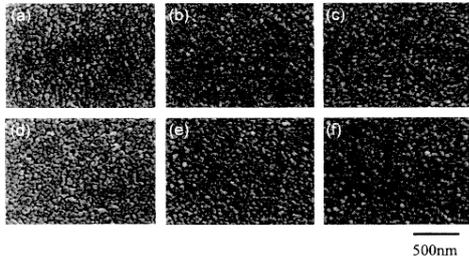


Fig. 1. SEM photographs of (a) before and (b-f) after etching of SiO₂ aerogel films for (b) 10, (c) 30, (d) 50, (e) 70, and (f) 90 sec.

of all energy regions of interest were recorded in order to quantify the film surface composition and to identify the elemental bonding states with pass energy of 20 eV. The angle-resolved XPS technique was used to analyze non-destructively the depth distribution of composition and bonding states by varying the take-off angle between 30° and 90° at intervals of 15°. For quantitative analyses, atomic sensitivity factors of Si, O, F, and C were obtained from standard specimens such as SiC, SiO₂, CF₂-teflon.

III. RESULTS AND DISCUSSION

The porosity of SiO₂ aerogel film was about 70 %. The ratio of Si, O, and C, *i.e.* the composition of the film, is 1:2.5:0.9. Also, the internal surface of the films was revealed to be covered with many hydroxyl (-OH) and organic (-OR; R=C₂H₅, CH₃, *etc.*) groups [1]. Fig. 1 corresponds to the images of SiO₂ aerogel films and it shows clearly a 3-dimensional network structure of the film. Fig. 1(a) is an image of the film before etching and (b), (c), (d), (e), and (f) are obtained after etching for 10, 30, 50, 70, and 90 sec, respectively. In these observations, 3-dimensional network structure of the film was

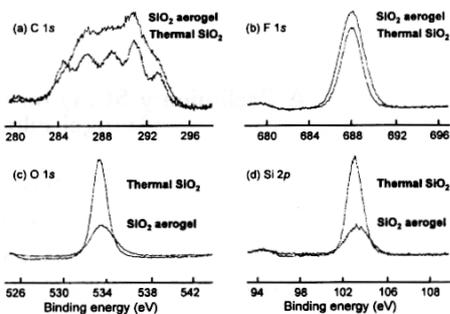


Fig. 2. XPS narrow scan spectra of 50 % etched SiO₂ aerogel and thermal SiO₂ films; (a) C 1s, (b) F 1s, (c) O 1s, and (d) Si 2p.

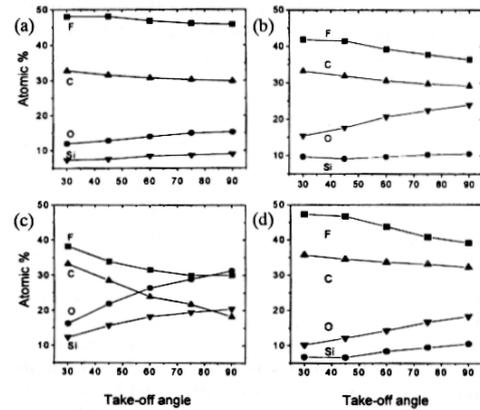


Fig. 3. Take-off angle dependency of surface compositions after (a), (c) 50 % etching, and (b), (d) 50 % over-etching of SiO₂ aerogel and thermal SiO₂ films, respectively.

preserved during etching in spite of its highly porous structure with 70 % porosity. Under our experimental condition, etch rate of thermally grown SiO₂ film was 1,300~1,350 Å/min and with SiO₂ aerogel film, it was 6,300~7,300 Å/min. This apparent-etch rate of SiO₂ aerogel film turned out to be 1,900~2,200 Å/min when the porosity of the film was counted. This is not quite a high value considering the porous nature of the film which may induce 3-dimensional etching instead of 2-dimensional etching of thermally grown SiO₂ film. Etching seemed to be disturbed by internal surface chemicals. The facts that real-etch rate of SiO₂ aerogel film was not relatively high and its microstructure was not changed during the etching means that macroscopically, SiO₂ aerogel film was not etched 3-dimensionally.

XPS narrow scan spectra of 50 % etched SiO₂ aerogel and thermally grown SiO₂ films are given in Fig. 2. The amounts of C and F are larger in SiO₂ aerogel than in

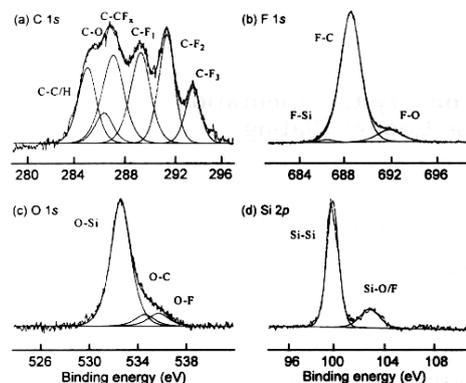


Fig. 4. Deconvolutions of narrow scan spectra obtained after 50 % over-etching of SiO₂ aerogel film; (a) C 1s, (b) F 1s, (c) O 1s, and (d) Si 2p.

thermally grown SiO₂. This means that there is thicker polymeric residue composed of C and F on the surface of SiO₂ aerogel film. Fluorine did not seem to be effective in breaking Si-O bond to form volatile Si-F products. This can be explained as follows. Hydrogen consisting of the internal surface of SiO₂ aerogel reacts with F to form HF. So, the concentration of active F decreases which in turn decelerates the etching process. Then, due to the decrease in etch rate, thick polymer residue layer could be formed. In Figs. 2(c) and (d), enlarged full width at half maximum (FWHM) of Si 2*p* and O 1*s* peaks in SiO₂ aerogel is observed due to the various surface bonding states such as hydroxyl and organic groups.

In Fig. 3, comparative surface compositions after the etching of SiO₂ aerogel and thermally grown SiO₂ films are plotted. Figs. 3(a) and (c) are obtained after 50 % etching of the films, and (b) and (d) are obtained after 50 % over-etching of the films, respectively. The observed amounts of F and C with 50 % etched thermally grown SiO₂ (Fig. 3(c)) are smaller than those with 50 % etched SiO₂ aerogel (Fig. 3(a)) and they sharply decrease with the increase in take-off angle. This means that a several nm of residue layer containing F and C exists on the top surface of 50 % etched thermally grown SiO₂ film. But, with 50 % etched SiO₂ aerogel, the intensity of observed photoelectron peaks is almost uniform even with the variation of take-off angle. This reflects the porous nature of SiO₂ aerogel, where the etching species combine with aerogel surface 3-dimensionally at minimum within the inelastic mean free path of the emitted photoelectrons. The ions and radicals of etching gas are impinged and diffused through the porous media.

After 50 % over-etching of the films, they show a similar change in atomic composition with take-off angle. Also, the thickness of residue layer for each films after the over-etching is almost same.

To investigate the chemical bonding states of surface residue on over-etched SiO₂ aerogel, narrow scan spectra were decomposed and the results are given in Fig. 4. There are C-F₃, C-F₂, C-F₁, C-CF_{*x*}, C-O, and C-C/H bondings in C 1*s* peak from high binding energy. F 1*s* peak is decomposed to F-Si, F-C, and F-O bondings. O 1*s* peak contains O-Si, O-C, and O-F bondings and Si 2*p* peak is composed of Si-Si and Si-O/F bondings [4,5].

As a result, unless the internal surface chemical bondings of SiO₂ aerogel affect the etch rate during etching,

but they could be removed effectively by CHF₃ plasma etching. There was no interruption during etching due to the accumulation of internal surface organics during the process. Also, the ultra thin residue layer with thickness of 3~4 nm observed after over-etching of SiO₂ aerogel film could be easily removed by conventional post-treatment [4].

IV. CONCLUSIONS

Through the angle-resolved XPS analyses, it was revealed that the etching constituents penetrated and mixed-up with SiO₂ aerogel internal surface within several nm thickness. But even with the porous nature of SiO₂ aerogel film, 3-dimensional etching which could collapse the network structure of the film did not occur. This was due to fluorine consumption reaction of internal surface chemicals in SiO₂ aerogel such as hydroxyl and organic groups. Also, these surface chemicals decreased the etch rate of SiO₂ aerogel. After over-etching of SiO₂ aerogel film, typical residue layer which could be obtained after over-etching thermally grown SiO₂ was obtained. From the above results, SiO₂ aerogel film with low dielectric constant could easily be adapted to a conventional etching process.

ACKNOWLEDGMENTS

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program Year 1998.

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