SHORT COMMUNICATION

Thickness of a Modified Surface Layer Formed in a Silsesquioxane-based Low-k Material During Etching in a Fluorocarbon Plasma

Sung-Wook Hwang, Gyeo-Re Lee, Jae-Ho Min and Sang Heup Moon[†]

School of Chemical Engineering and Institute of Chemical Processes, Seoul National University,
San 56-1, Shillim-dong, Kwanak-ku, Seoul 151-744, Korea

Abstract—This paper explains the origin of our previous observation that, when a silsesquioxane-based low-k film is etched in fluorocarbon plasmas, the thickness of a surface modified layer, in which cage-like Si-O bonds are dissociated to extents greater than a specified level, changes linearly with $\log[F]^2/[CF_2]$, where $[F]$ and $[CF_2]$ denote concentrations of F and CF_2 radicals in the bulk plasma. During the etching process, the substrate consists of three distinct layers: a fluorocarbon layer, a modified surface layer, and an unmodified layer. F density at the interface between the fluorocarbon and the modified surface layers, denoted as F_0 in this study, is determined in proportional to $[F]^2/[CF_2]$, and the density decreases exponentially with the film depth. As a result, the thickness of the modified surface layer changes in proportion to a parameter, $\log[F]^2/[CF_2]$.

Key words: Low-k Material, Silsesquioxane, Plasma Etching, Fluorocarbon, Surface Layer

MAIN TEXT

In the recent fabrication technology of integrated circuits, low dielectric constant (low-k) materials are used to solve an RC delay problem in interconnects. Introduction of low-k materials requires the etching of complex structures and, accordingly, it is important to understand the etch characteristics of low-k materials, in order to better control the etch process and eventually obtain desirable etch profiles.

In our previous study [Hwang et al., 2002], we investigated etch reaction pathways of a silsesquioxane-based low-k material in fluorocarbon plasmas and demonstrated that cage-like Si-O bonds, which constitute characteristic bonds of silsesquioxane-based low-k materials along with network Si-O bonds and play a key role in lowering the dielectric constant, were readily dissociated by reaction with F radicals even under process conditions of low ion energy. As a result, the surface of the low-k material exposed to a fluorocarbon plasma was modified such that the amounts of cage-like Si-O bonds in the layer were smaller than those contained in the original material. By correlating the amounts of Si-O bonds retained in the substrate with concentrations of radicals in the bulk plasma under various process conditions, it was finally proposed that the thickness of the modified surface layer was linearly proportional to $\log[F]^2/[CF_2]$, where $[F]$ and $[CF_2]$ denote concentrations of F and CF_2 radicals in the bulk plasma and were measured by actinometry using optical emission spectroscopy (OES) [Coburn et al., 1980]. However, this linear relation was empirically obtained just by a fitting method and the basis of the above relation was not clear in the previous study and, accordingly, we carried out this study to better understand the origin of the relation based on experimental evidence.

Hydrido-organo-siloxane-polymer (HOSP), a typical silsesquioxane, was spin-coated on a p-type Si wafer, and sequentially baked

on a hot plate at 150, 200, and 350 °C for 1 min to eliminate solvent inside the film. After baking, the wafer was cured at 400 °C for 1 h in an N_2 atmosphere.

Etching experiments were implemented in a transformer coupled plasma (TCP) etcher, which was previously described [Cho et al., 1999]. CHF_3 was used as an etching gas and was supplied at 5 sccm through a gas diffuser. The pressure was fixed at 10 mTorr, a source power at 600 Watt, a bias voltage at −100 V, and the cathode temperature at 15 °C. Samples, 1.5 cm×1.5 cm in size, were placed and etched on an Si wafer, which, in turn, was fixed to the
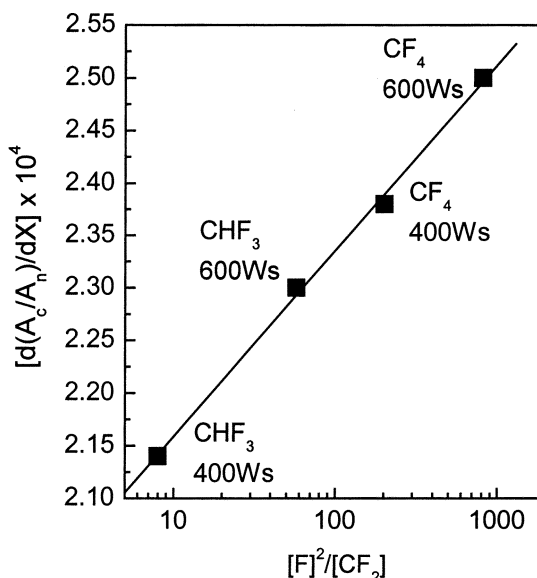

Fig. 1. Peak area ratios of cage-like Si-O and network Si-O bonds contained in HOSP film etched in fluorocarbon plasmas under various process conditions as a function of (F radical density)²/(CF₂ radical density) in the bulk plasma. Cited from [Hwang et al., 2002].

[†]To whom correspondence should be addressed.
E-mail: shmoon@surf.snu.ac.kr

cathode. After partial etching, the F depth profile of the film was obtained by Auger electron spectroscopy.

Fig. 1, presented in our previous study [Hwang et al., 2002], shows that $d(A_c/A_n)/dX$ changes linearly with $\log[F]^2/[CF_2]$. Here, A_c and A_n mean the amounts of cage-like Si-O bond and network Si-O bond peak obtained in infrared spectra of the substrate, and X is the thickness of a HOSP film after etching. Each value of $d(A_c/A_n)/dX$ was obtained from a plot of A_c/A_n's for different X values obtained by varying the etch time under the same process condition. This plot shows a linear relation between A_c/A_n and X. The slope, $d(A_c/A_n)/dX$, means the relative dissociation rates of cage-like Si-O and network Si-O bonds, i.e., the extent of modification in the surface layer.

During etching with fluorocarbon plasmas, the substrate consists of three layers as schematically shown in Fig. 2: a fluorocarbon layer, a modified surface layer, and an unmodified layer. These layers are under a steady state as a result of balance between etching and deposition (or diffusion in the case of a modified surface
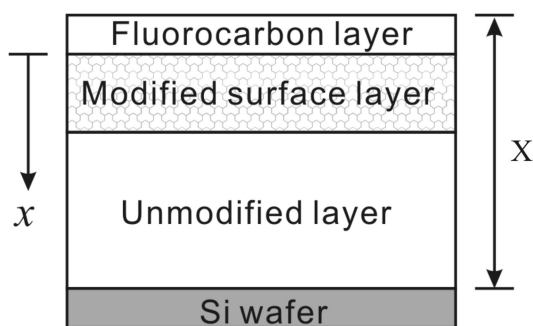

Fig. 2. Schematic diagram of cross-section of a HOSP film after etching in a fluorocarbon plasma. x denotes the depth into the etched HOSP film from the surface and X denotes the thickness of a HOSP film remaining after etching.
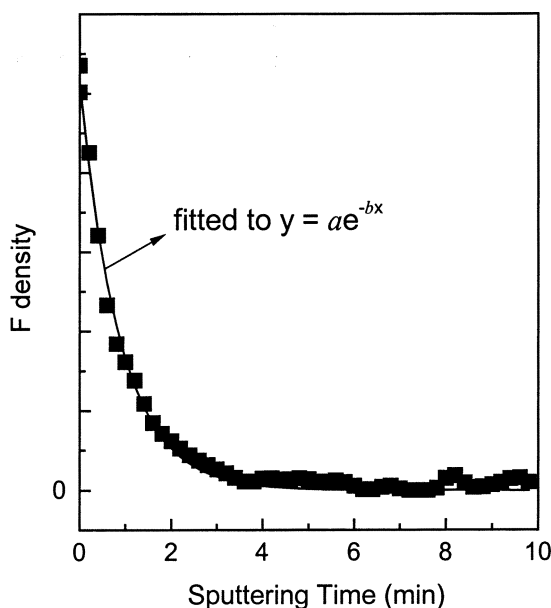

Fig. 3. Depth profile of F concentration in a HOSP film etched in a CHF₃ plasma: the chamber pressure at 10 mTorr, a source power at 600 Watt, and a bias voltage at −100 V.

layer) [Rueger et al., 1997]. Thickness of the fluorocarbon layer has been reported to be proportional to $[CF_2]$ and inversely proportional to $[F]$ in the bulk plasma [Zhang and Kushner, 2001] and, as a result, the diffusion rate of F radicals through the fluorocarbon layer should change linearly with $[F]/[CF_2]$. This means that F density at the interface between the fluorocarbon layer and the modified surface layer, F_0, is proportional to $[F]^2/[CF_2]$, i.e., the multiplication of F radical concentration in the bulk plasma, $[F]$, and the diffusion rate of F radicals, $[F]/[CF_2]$.

Fig. 3 shows the depth profile of F density in the HOSP film etched in a CHF₃ plasma, which was obtained by Auger electron spectroscopy after removal of the fluorocarbon layer. F density decreases exponentially with an increase in the depth and it can be expressed as the following.

$$F(x) = a\, F_0 \exp(-bx) \tag{1}$$

where x is the depth into the film and a and b are positive constants.

Modification in the surface layer is mainly caused by F radicals because cage-like Si-O bonds are rapidly dissociated by reaction with F radicals, whereas the dissociation of network Si-O bonds requires CF₂ radicals and high ion energy as well as F radicals. Therefore, it is reasonable to assume that there is a minimum F density required for the modification of HOSP film, F_m. Accordingly, x_m, which is the film depth corresponding to the F density of F_m, is the deepest point in the HOSP film, where the dissociation of cage-like Si-O bonds occurs to a minimum level. This leads to the transformation of Eq. (1) into

$$F_m = a\, F_0 \exp(-bx_m) \tag{2}$$

or

$$x_m = c \log F_0 + d. \text{ (c, d: positive constants)} \tag{3}$$

As mentioned earlier, F_0 is proportional to $[F]^2/[CF_2]$ and therefore Eq. (3) can be described as

$$x_m = c \log [F]^2/[CF_2] - d' \text{ (d': positive constant)} \tag{4}$$

Here, x_m can be regarded as the thickness of a modified surface layer in the HOSP film obtained after etching in a fluorocarbon plasma because cage-like Si-O bonds in the HOSP film are very rapidly dissociated by reaction with F radicals compared to the case of network Si-O bonds. The y-axis variable of Fig. 1, $d(A_c/A_n)/dX$ is simply proportional to the variation of cage-like Si-O bonds included in the HOSP film after etching because parameters A_n and X remain nearly constant independent of parameters $[F]$ and $[CF_2]$, which constitute the x-axis variable. That is, the reaction rate of network Si-O bonds with either F or CF₂ radicals is much slower than that of cage-like Si-O bonds with F radicals, as explained in the above, and the substrate thickness, X, is determined largely by etch time instead of the radical concentrations.

In conclusion, the origin of a linear relation between the relative dissociation rates of cage-like Si-O bonds to those of network Si-O bonds, $d(A_c/A_n)/dX$, and a parameter related to radical concentrations in the bulk plasma, $\log[F]^2/[CF_2]$, has been explained, with the aid of F depth profiling data.

The relative amounts of cage-like Si-O and network Si-O bonds remaining in the HOSP film after etching are important because they are closely related to the properties of the film. It is obviously

desirable that the etched film maintains the same content of cage-like Si-O bonds as was present before etching such that the initial property of the HOSP film is preserved. The results of this study indicate that a HOSP film etched under conditions of high $[F]^2/[CF_2]$ values is subject to the decomposition of cage-like Si-O bonds to a greater extent than that of network Si-O bonds and, as a result, exhibits a composition significantly deiviated from the initial value. In this respect, the relative amounts of two Si-O bonds present in the film after etching can be maintained close to those before etching by employing plasma conditions that provide low $[F]^2/[CF_2]$ values.

ACKNOWLEDGMENT

REFERENCES

Cho, B.-O., Hwang, S.-W., Ryu, J.-H. and Moon, S. H., "More Vertical Etching Profile Using a Faraday Cage in Plasma Etching," *Rev. Sci. Instrum.*, **70**, 2458 (1999).

Coburn, J. W. and Chen, M., "Optical Emission Spectroscopy of Reactive Plasmas: A Method for Correlating Emission Intensities to Reactive Particle Density," *J. Appl. Phys.*, **51**, 3134 (1980).

Hwang, S.-W., Lee, G.-R., Min, J.-H., Moon, S. H., Kim, Y. C., Ryu, H.-K., Cho, Y. S. and Kim, J. W., "Etch Characteristics of Silsesquioxane-based Low Dielectric Constant Material in Fluorocarbon Plasma," *Jpn. J. Appl. Phys.*, **41**, 5782 (2002).

Rueger, N. R., Beulens, J. J., Schaepkens, M., Doemling, M. F., Mirza, J. M., Standaert, T. E. F. M. and Oehrlein, G. S., "Role of Steady State Fluorocarbon Films in the Etching of Silicon Dioxide Using CHF3 in an Inductively Coupled Plasma Reactor," *J. Vac. Sci. Technol.*, A **15**, 1881 (1997).

Ryu, J.-H., Cho, B.-O., Hwang, S.-W., Moon, S. H. and Kim, C.-K., "Trajectories of Ions Inside a Faraday Cage Located in a High Density Plasma Etcher," *Korean J. Chem. Eng.*, **20**, 407 (2003).

Zhang, D. and Kushner, M. J., "Investigations of Surface Reactions during C_2F_6 Plasma Etching of SiO_2 with Equipment and Feature Scale Models," *J. Vac. Sci. Technol.*, A **19**, 524 (2001).