

## Study of ashing for low-k dielectrics using the N<sub>2</sub>/O<sub>2</sub> ferrite-core inductively coupled plasmas

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### Abstract

We have studied the characteristics of photoresist (PR) ashing using N<sub>2</sub>/O<sub>2</sub> plasmas in ferrite-core inductively coupled plasma etcher. By varying the O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio, we have changed the PR ash rate and the low-k material etch rate, obtaining the PR ash rate and the PR to low-k materials etch selectivity, respectively, of 15,000 Å/min and 180. Fourier transform infrared spectroscopy and HF etch test coincidentally indicated that the ash damage to the low-k material decreased with decreasing the O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio.

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### 1. Introduction

In order to fully take advantage of copper interconnects in semiconductor devices, low-k dielectric material must be used to reduce interelectrode capacitance. Since the chemical structure of many low-k materials differs from and is less passive than that of the conventional SiO<sub>2</sub> dielectric, standard photoresist (PR) ashing process using O<sub>2</sub> plasmas in the conventional asher can cause unacceptable undercutting due to insufficient selectivity and can fundamentally alter the properties of low-k material by generating the damage layer [1–5], defeating the purpose of using a low-k material film.

Accordingly, in developing the ashing technology for low-k material films, in order to reduce the oxygen diffusion into the low-k dielectric film, researchers have investigated

the feasibility of introducing the oxygen-free plasmas such as N<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>/H<sub>2</sub>, and NH<sub>3</sub> [5–7]. However, the addition of non-O<sub>2</sub> chemistry suffers from the reduction of ash rate. In the present work, we report the characteristics of PR ashing process using the N<sub>2</sub>/O<sub>2</sub> gas mixture in the inductively coupled plasma (ICP) system with a ferrite-core. Although several researchers have studied on the properties and applications of the ferrite-core [8–10], to our knowledge, the application of the ferrite-core system to the plasma etching or ashing process has not been reported to date. We have investigated the ashing damage of low-k material by HF dipping technique and Fourier transform infrared (FTIR) spectroscopy.

### 2. Experiments

The equipment used in this study is an ICP-type etcher with a ferrite-core (Fig. 1). Although the detailed study is

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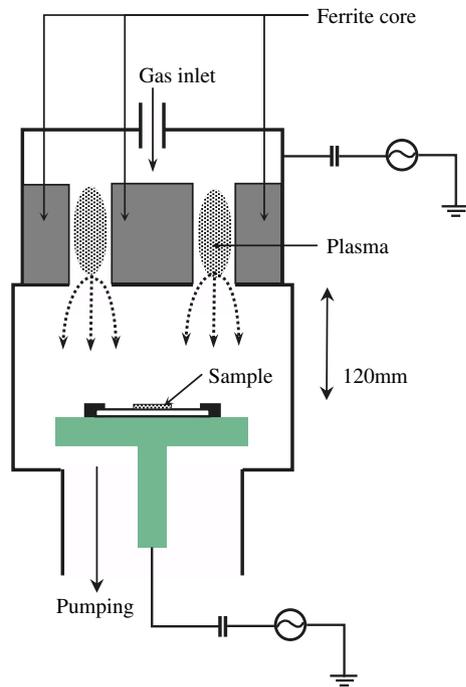


Fig. 1. Schematic diagram of experimental apparatus.

underway [11], the installed ferrite-core is expected to help to obtain a higher plasma density, compared to that of the conventional ICP. During the ashing process, the source power was 6000 W with a frequency of 400 kHz, the bias power was 400 W with a frequency of 13.56 MHz, the pressure was 1.1 Torr and the total gas flow rate was 4000 sccm. The samples were situated on the center of the wafer, which was held on a mechanical chuck. The 13.56 MHz RF bias power supply was coupled to the electrode to extract ions from the plasma.

The ashing material was a PR (SRK-01, Tokyo Ohka Kogyo Co., Japan) on the silicon (Si) substrate. Also, the Si substrates were coated with a 4000-Å-thick layer of low-k materials (SiOCH) with the as-deposited dielectric constant of 2.8, by the chemical vapor deposition method at temperatures in the range of 350–400 °C. The chemical bonds of the low-k material films after different ashing processes were investigated by FTIR spectroscopy (Bruker-IFS66 V/S). In addition, film degradation was evaluated by treating with 50% aqueous HF solution for 5 s. Immediately after the HF dipping, the samples were dipped and rinsed in deionized water. Only a part of the ashed samples was soaked into the HF solution and subsequently alpha-step profilometer was used to measure the difference of film height between the soaked and the unsoaked regions.

### 3. Results and discussion

In order to investigate the ashing characteristics using ferrite-core ICP, we have varied the  $O_2/(O_2+N_2)$  gas flow ratio. Fig. 2a shows the changes of PR ash rate and low-k

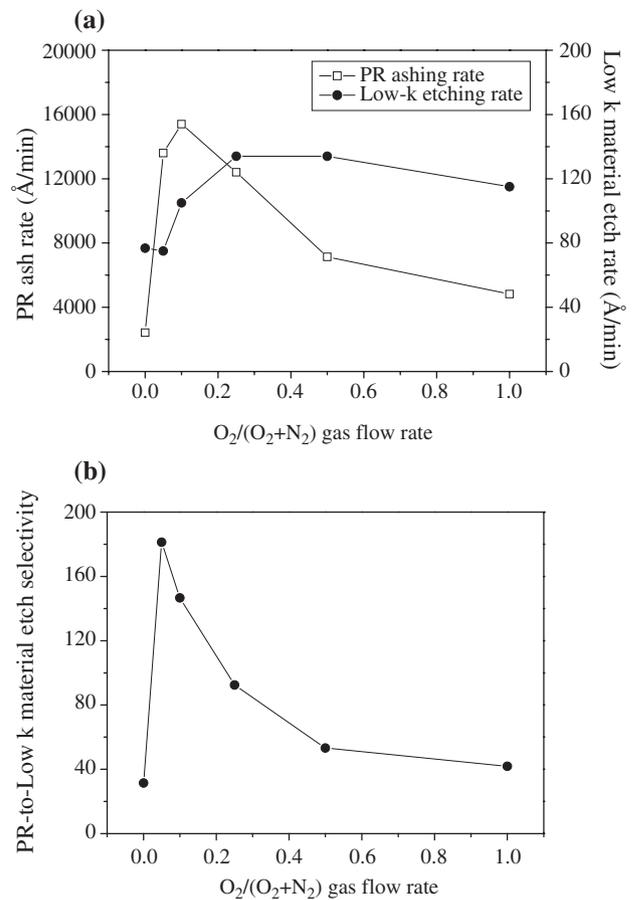


Fig. 2. (a) Variation of the PR ash rate and the low-k material etch rate and (b) variation of the PR to low-k material etch selectivity with varying  $O_2/(O_2+N_2)$  gas flow ratio in the range of 0–1.

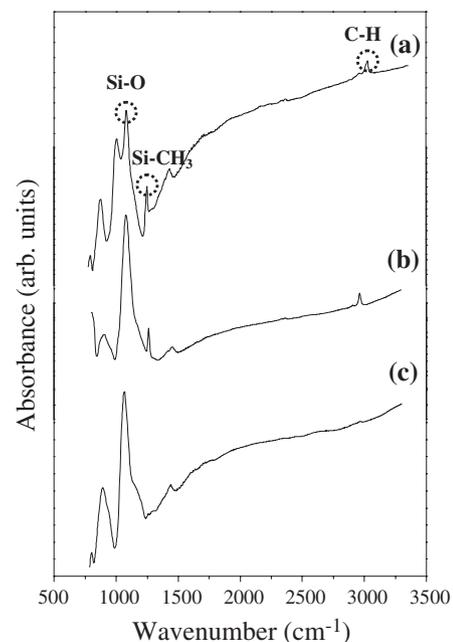


Fig. 3. FTIR absorbance spectra of the low-k material films after the ashing process with  $O_2/(O_2+N_2)$  gas flow ratio of (a) 0, (b) 0.25, and (c) 1.

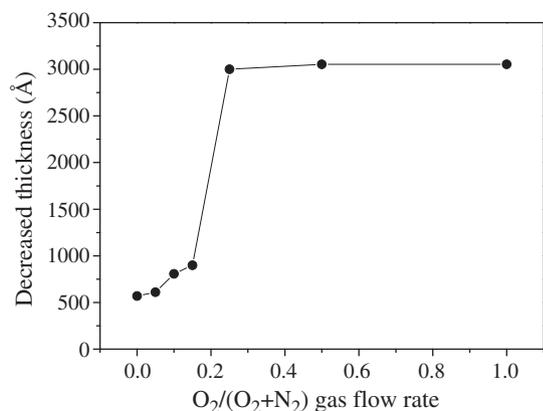


Fig. 4. Decreased thicknesses of the low-k material films by the HF dipping treatment, depending on the previous ashing process with various O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratios.

material etch rate with varying O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio in the range of 0–1, revealing that the PR ash rate has its maximum value at O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio in the range of 0.05–0.25. With the O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio of 0.1, the PR ash rate of about 15,000 Å/min is attained. On the other hand, the etch rate of low-k material is measured to be below 150 Å/min, regardless of the gas flow ratio. Fig. 2b shows the variation of PR to low-k material etch selectivity with varying O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio in the range of 0–1, revealing that the high selectivity of about 180 is obtained at O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio of 0.05.

We have investigated the chemical-bonding characteristics of the low-k materials films using FTIR absorbance analysis. Fig. 3 shows the FTIR absorbance spectra of the low-k material films after the ashing process with various O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio. The spectra exhibit Si–O, Si–CH<sub>3</sub>, and C–H absorption peaks, respectively, centered at 1080, 1270, and 2970 cm<sup>-1</sup>. The relative intensities of C–H and Si–CH<sub>3</sub> peaks compared to the Si–O peak increase with decreasing O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio. We surmise that during O<sub>2</sub> plasma ashing, the Si–CH<sub>3</sub> and C–H bonds in the films are readily attacked and broken by the active oxygen species of the plasma discharge, and subsequently replaced by Si–O bonds, resulting in a more SiO<sub>2</sub>-like film with a high dielectric constant. On the other hand, the role of nitrogen may be to dilute the effects of the oxygen species in the plasma and/or to generate the nitrogen containing layer which acts as a barrier against the ashing damage [12]. Further study is necessary to disclose the detailed mechanism.

In order to evaluate the degradation of low-k material film by the ashing process, we have applied the HF dipping test. Fig. 4 shows the decreased thicknesses of the low-k material films by the HF dipping treatment (i.e. the difference of low-k material film thickness before and after the HF dipping) depending on the previous ashing process with various O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio. The decreased thicknesses of the samples after the HF dipping, which were previously ashed with O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio of 0, 0.05,

0.1, 0.15, 0.25, 0.5 and 1, respectively, are measured to be 570, 610, 810, 900, 3000, 3050 and 3050 Å. While about 3000-Å-thick films have been removed by the HF dipping for the materials ashed with the O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio in the range of 0.25–1, less than 1000-Å-thick films have been removed for those ashed with the ratio in the range of 0–0.15. It is noteworthy that the amount of removed material by the HF dipping slightly increases with increasing the O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio in the range of 0–0.15 but the amount significantly increases with increasing the O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio from 0.15 to 0.25.

Since the damaged layer is the region where the Si–CH<sub>3</sub> and C–H bonds have been broken and thus was changed to the SiO<sub>2</sub>-like material, it is easily etched by the HF solution, while the original low-k material is not. Therefore, the decreased thickness by the HF dipping is close to the thickness of the damaged layer. We conclude that the thickness of damaged layer increases with increasing the O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio in the present ashing process, agreeing with FTIR spectra.

#### 4. Conclusion

We have presented a first study of photoresist ashing using a ferrite-core ICP. We reveal that the O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio significantly affects the PR ash rate and the ashing damage. With the O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio in the range of 0.05–0.1, we have obtained the PR ash rate and the PR to low-k materials etch selectivity, respectively, of 15,000 Å/min and 180. The employment of the ashing process with the lower O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>) gas flow ratio generates the less ashing damage.

#### References

- [1] T.C. Chang, P.T. Liu, Y.J. Mei, Y.S. Mor, T.H. Perng, Y.L. Yang, S.M. Sze, *J. Vac. Sci. Technol.*, B 17 (1999) 2325.
- [2] P.T. Liu, T.C. Chang, Y.S. Mor, S.M. Sze, *Jpn. J. Appl. Phys.* 38 (1999) 3482.
- [3] S.A. Vitale, H.H. Sawin, *J. Vac. Sci. Technol.*, A 20 (2002) 651.
- [4] Y.H. Kim, H.J. Kim, J.Y. Kim, Y. Lee, *J. Korean Phys. Soc.* 40 (2002) 94.
- [5] K. Yonekura, S. Sakamori, K. Goto, M. Matsuura, N. Fujiwara, M. Yoneda, *J. Vac. Sci. Technol.*, B 22 (2004) 548.
- [6] T. Kropewnicki, M. Dahimene, J. Pender, H. Nguyen, H. Fong, R. Hung, C. Björkman, *Proceedings of the 23rd Symposium on Dry Process*, 2001, p. 235.
- [7] H. Nambu, A. Nishizawa, E. Soda, T. Maruyama, K. Tokashiki, *Proceedings of the 24th Symposium on Dry Process*, 2002, p. 15.
- [8] E.L. Boyd, *J. Appl. Phys.* 39 (1968) 1304.
- [9] F.G. Hewitt, *J. Appl. Phys.* 40 (1969) 1464.
- [10] K. Takata, F. Tomiyama, Y. Shiroishi, *J. Magn. Mater.* 269 (2004) 131.
- [11] D.-K. Choi, applied for a U.S. patent (Appl. No. 10-2002-63298).
- [12] T.C. Chang, Y.S. Mor, P.T. Liu, T.M. Tsai, C.W. Chen, Y.J. Mei, S.M. Sze, *Thin Solid Films* 398–399 (2001) 632.