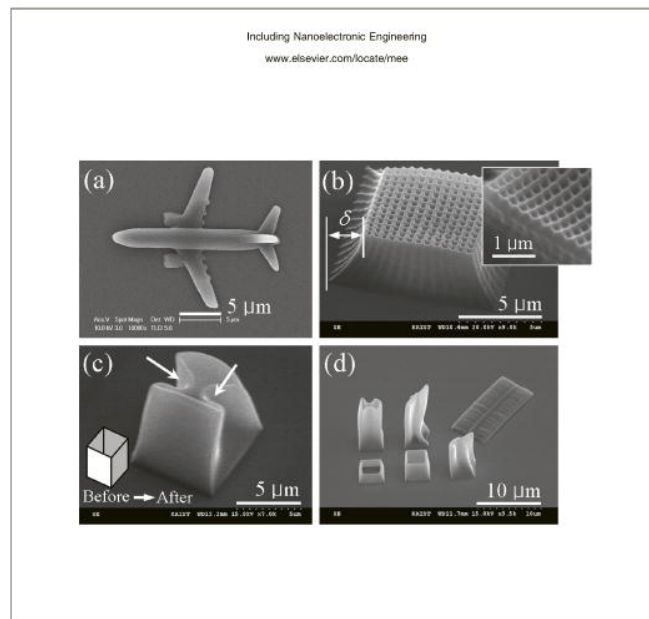




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Etching characteristics of photoresist and low- k dielectrics by Ar/O₂ ferrite-core inductively coupled plasmas

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Abstract

We have investigated the characteristics of Ar/O₂ plasmas in terms of the photoresist (PR) and low- k material etching using a ferrite-core inductively coupled plasma (ICP) etcher. We found that the O₂/(O₂+ Ar) gas flow ratio significantly affected the PR etching rate and the PR to low- k material etch selectivity. Fourier transform infrared spectroscopy (FTIR) and HF dipping test indicated that the etching damage to the low- k material decreased with decreasing O₂/(O₂+ Ar) gas flow ratio.

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1. Introduction

Since resistance–capacitance delay in metal interconnects becomes a serious problem at high clock frequencies, low- k ($k \leq 2.9$) dielectric materials have been introduced as interlayer dielectric materials for ultra-large-scale integrated (ULSI) circuits. Because many low- k materials contain a significant amount of methyl (CH₃) groups and are less passive than conventional SiO₂ dielectric, a standard photoresist (PR) ashing process using O₂ plasmas in a

conventional asher can fundamentally alter the properties of a low- k material by generating a damaged layer [1–5]. This in turn raises the capacitance of the low- k material even beyond that of SiO₂ dielectric materials. Consequently, there has been renewed interest in solving problems associated with the ashing process by providing high PR to dielectric etch selectivity, while leaving the k -value of the low- k dielectric materials unaffected. To date, although the addition of non-O₂ chemistry causes a reduction of the PR etching rate, the feasibility of introducing non-O₂ gases such as N₂, H₂, N₂/H₂, and NH₃ to the PR etching process has been studied in efforts to reduce oxygen diffusion into low- k dielectric films [5–7].

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In the present work, we investigate the characteristics of PR etching processes by using an O_2/Ar gas mixture, for potential application to ULSI processes. This approach is motivated by the finding that the O_2/Ar etching process generates more vertical and uniform PR profiles than a pure O_2 etching process [8]. The process was carried out at room temperature without external heating, because PR etching at lower temperatures is expected to significantly improve the PR etching uniformity. We have employed an inductively coupled plasma (ICP) system with ferrite-cores [9–12], which is different from the conventional advanced plasma sources [13,14]. By installing ferrite-cores wound within an ICP antenna, the ferrites, having a sufficiently high magnetic permeability, help to provide a high enough electric field for generating plasmas. Compared to conventional ICP, the ferrite-core ICP has advantages such as high plasma efficiency, low power consumption, and adaptability to large-area applications. To the best of the authors' knowledge, this is the first report not only on the utilization of a ferrite-core ICP with Ar/O_2 plasmas, but also on the application of Ar/O_2 plasmas to the PR etching process for low- k dielectrics. The addition of Ar to O_2 plasmas is expected to reduce the degradation of low- k material, whereas the ferrite-core ICP is employed in compensation for the reduction of PR etching rate in the present Ar -diluted and low-temperature process. We have investigated etching damage to low- k material by Fourier transform infrared (FTIR) spectroscopy and a HF dipping technique.

2. Experiment

The experimental apparatus used in the present study is illustrated in Fig. 1 [15]. The source power is supplied by passive transformers and coils that use ferrite cores with

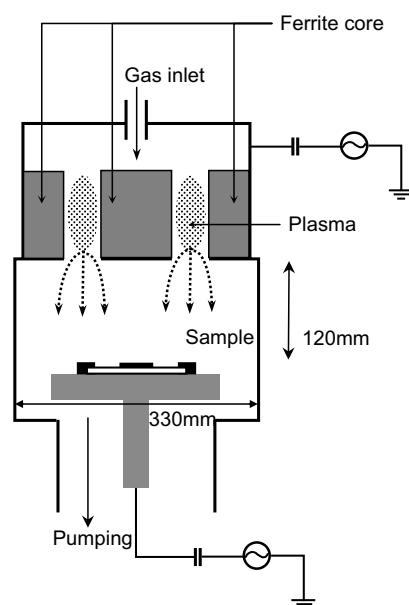


Fig. 1. Schematic diagram of ferrite-core ICP etcher.

magnet-wire windings (not shown in the figure). The etching was performed at a source power, bias power, pressure, and the total gas flow rate of 6000 W (with a frequency of 400 kHz), 400 W (with a frequency of 13.56 MHz), 1.1 Torr, and 4000 sccm, respectively. The process was carried out at room temperature, without intentional heating. The sample was located on the center of the substrate holder. The bottom electrode was powered by a 13.56 radio-frequency (rf) source through an impedance matching network.

In order to measure the PR etching rate, we used a PR (SRK-01, Tokyo Ohka Kogyo Co., Japan) on the silicon (Si) substrate. For investigation of the etching rate and etching damage to the low- k material, we used a 4000 Å-thick layer of low- k materials ($SiOCH$) with a dielectric constant (k -value) of 2.8. $SiOCH$ was coated on a Si substrate by chemical vapor deposition in a temperature range of 350–400 °C. The chemical structure of the low- k material films was studied using FTIR spectroscopy (Bruker-IFS66 V/S). Additionally, degradation of the low- k material films was evaluated via treatment with a 50% aqueous HF solution. Immediately after HF dipping for 5 s, the samples were dipped and rinsed in deionized water. Only a portion of the etched low- k material film was soaked into the HF solution. An alpha-step profilometer was subsequently used to measure the difference in the film height between the soaked and unsoaked regions.

3. Results and discussion

Fig. 2a shows the changes of PR etching rate and low- k material etching rate with varying $O_2/(O_2 + Ar)$ gas flow ratio in a range of 0–1, revealing that the PR etching rate tends to increase with increasing $O_2/(O_2 + Ar)$ gas flow ratio. With a $O_2/(O_2 + Ar)$ gas flow ratio of 0.75, we obtained a PR etching rate of 6720 Å/min. Previously, PR etching experiments using an Ar/O_2 system were carried out using a conventional ICP etcher with a PR pattern trimming rate of less than 1000 Å/min [8] and by using a dielectric barrier discharge etcher with a maximum PR etching rate of 1900 Å/min [16]. Fig. 2a indicates that the etching rate of the low- k material is below 200 Å/min, regardless of the $O_2/(O_2 + Ar)$ gas flow ratio. Fig. 2b shows the variation of PR to low- k material etch selectivity with varying $O_2/(O_2 + Ar)$ gas flow ratio, indicating that a high selectivity of approximately 84 is obtained at an $O_2/(O_2 + Ar)$ gas flow ratio of 0.75.

Fig. 3 shows the FTIR spectra for the low- k material films after the etching process with various $O_2/(O_2 + Ar)$ gas flow ratios. The spectra exhibit Si–O, Si–CH₃, and C–H absorption bands, peaked at 1080, 1270, and 2970 cm^{-1} , respectively (indicated by dotted circles in Fig. 3a). A comparison of Fig. 3d with Fig. 3a–c reveals that the relative intensities of C–H and Si–CH₃ peaks compared to the Si–O peak with a $O_2/(O_2 + Ar)$ gas flow ratio of 1 are significantly smaller than those with an $O_2/(O_2 + Ar)$ gas flow ratio of 0.25–0.75.

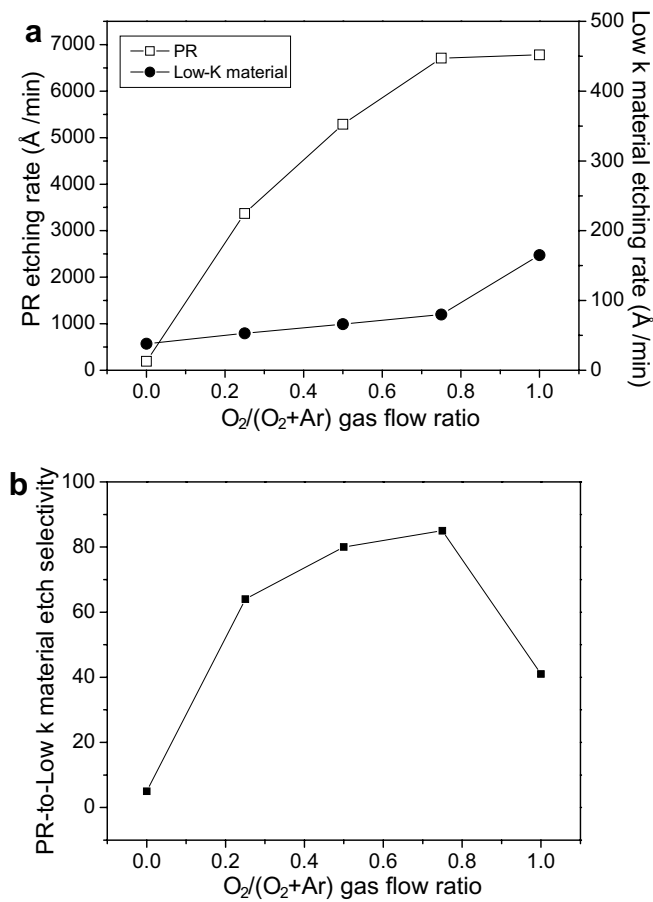


Fig. 2. (a) Changes of the PR and the low-*k* material etching rates and (b) changes of the PR to low-*k* material etch selectivity with varying $O_2/(O_2 + Ar)$ gas flow ratio.

Since the FTIR analysis does not precisely determine the degree of low-*k* material degradation at an $O_2/(O_2 + Ar)$ gas flow ratio in a range of 0.25–0.75, we carried out a HF dipping test. It is widely accepted that the damaged layer in low-*k* materials is the region where, the Si-CH₃ and C-H bonds have been broken and thus changed to a SiO₂-like material. Therefore, the damaged layer can be easily etched and removed by dipping into a HF solution, whereas the undamaged low-*k* material is not affected. This suggests that the reduction in thickness resulting from HF dipping is closely associated with the thickness of the damaged layer. Fig. 4 shows the variations in thicknesses of the low-*k* material films after HF dipping treatment (i.e. the difference of low-*k* material film thickness before and after HF dipping), where the $O_2/(O_2 + Ar)$ gas flow ratio of the previous etching process has been varied. The reduced thicknesses of the samples after HF dipping, which were previously etched with an $O_2/(O_2 + Ar)$ gas flow ratio of 0.25, 0.5 and 0.75, respectively, are measured to be 410, 2040, and 2320 Å. Thus, it is found that the amount of low-*k* material removed by HF dipping decreases with a decrease of the $O_2/(O_2 + Ar)$ gas flow ratio in a range of 0.25–0.75. Layers less than 500 Å in thickness were removed by HF dipping for the samples etched with an

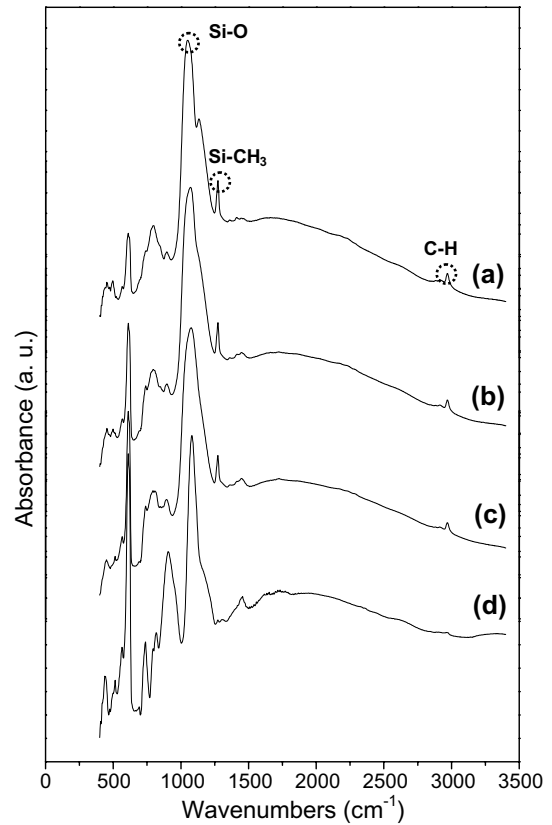


Fig. 3. FTIR spectra for the low-*k* material films after the etching process with an $O_2/(O_2 + Ar)$ gas flow ratio of (a) 0.25, (b) 0.50, (c) 0.75, and (d) 1.

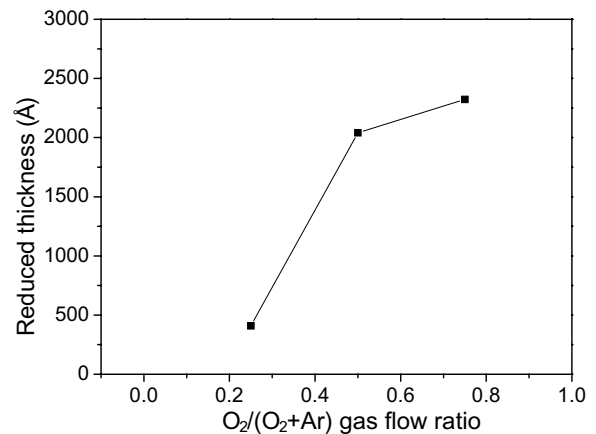


Fig. 4. Variation of reduced thicknesses of the low-*k* material films after HF dipping treatment with variation of the $O_2/(O_2 + Ar)$ gas flow ratio of the previous etching process.

$O_2/(O_2 + Ar)$ gas flow ratio of 0.25, whereas layers exceeding 2000 Å thickness were removed when etched with an $O_2/(O_2 + Ar)$ gas flow ratio in a range of 0.5–0.75. Accordingly, the HF dipping test reveals that the thickness of the damaged layer tends to decrease with decreasing $O_2/(O_2 + Ar)$ gas flow ratio.

In the present etching process, active oxygen species may preferentially attack and break the Si-CH₃ and C-H bonds

and replace them with Si–O bonds, particularly on the surface of the low- k material films, thus ultimately changing the low- k dielectric material to a SiO₂-like material. Although the underlying mechanism is not clear at this moment, it is noteworthy that replacing O₂ with Ar in the etching gas helps to reduce etching damage to low- k materials. It is possible that the addition of Ar to O₂ may lead to a change in the plasma characteristics as well as a transition of the etching mechanism from chemical to physical form. In order to elucidate the mechanism, we are planning to carry out plasma diagnostics measurements, and investigate the effects of Ar mixing ratio on plasma characteristics such as electron temperature, electron density, ion density, radical density, degree of dissociation, etc. Subsequently, we will correlate the plasma characteristics with the PR etching rate and surface properties of low- k materials. In order to monitor the changes in the surface characteristics of low- k material layers with varying etching chemistry, we will investigate the elemental depth profiles, chemical bonding states, and surface roughness.

4. Conclusions

In this study, we investigated the characteristics of PR ashing and low- k material etching at room temperature using a ferrite-core ICP. With an O₂/(O₂ + Ar) gas flow ratio of 0.75, we obtained a PR etching rate and PR to low- k materials etching selectivity of 6720 Å/min and 84, respectively. Employing the etching process with a lower O₂/(O₂ + Ar) gas flow ratio reduces etching damage to the low- k materials.

Acknowledgement

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References

- [1] S.A. Vitale, H.H. Sawin, *J. Vac. Sci. Technol. A* 20 (2002) 651.
- [2] Y.H. Kim, H.J. Kim, J.Y. Kim, Y. Lee, *J. Korean Phys. Soc.* 40 (2002) 94.
- [3] 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.
- [4] P.T. Liu, T.C. Chang, Y.S. Mor, S.M. Sze, *Jpn. J. Appl. Phys.* 38 (1999) 3482.
- [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] S. Mathew, R. Nagarajan, L.K. Bera, F.H. Hua, D.A. Yan, N. Balasubramanian, *Thin Solid Films* 462–463 (2004) 63.
- [9] S. Lloyd, D.M. Shaw, M. Watanabe, G.J. Collins, *Jpn. J. Appl. Phys.* 38 (1999) 4275.
- [10] E.L. Boyd, *J. Appl. Phys.* 39 (1968) 1304.
- [11] F.G. Hewitt, *J. Appl. Phys.* 40 (1969) 1464.
- [12] K. Takata, F. Tomiyama, Y. Shiroishi, *J. Magn. Magn. Mater.* 269 (2004) 131.
- [13] I. Ganachev, H. Sugai, *Surf. Coat. Technol.* 174–175 (2003) 15.
- [14] K. Hou, S. Nakagami, T. Makabe, *Thin Solid Films* 386 (2001) 239.
- [15] H.W. Kim, J.H. Myung, N.H. Kim, H.S. Lee, S.-G. Park, J.G. Lee, C.W. Chung, W.J. Park, C.-J. Kang, C.-G. Yoo, K.-H. Ko, J.-H. Woo, S.-D. Choi, D.-K. Choi, *Thin Solid Films* 506–507 (2006) 222.
- [16] M.-H. Jung, H.-S. Choi, *Thin Solid Films* 515 (2006) 2295.