Control of SiO₂ contact-hole etch profiles using low-GWP heptafluoropropyl methyl ether

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Abstract: Heptafluoropropyl methyl ether (HFE-347mcc3) as a lower-GWP (global warming potential) alternative to PFCs (perfluorocarbons) was used to etch SiO₂ contact holes. The etch profiles of the SiO₂ contact holes in HFE-347mcc3/O₂/Ar plasmas showed more bowing at lower flow rates of HFE-347mcc3, whereas more narrowing occurred at higher flow rates of HFE-347mcc3. By selecting the precise flow rates of HFE-347mcc3/O₂/Ar (9/2/19 sccm), a highly anisotropic profile of a SiO₂ contact hole was achieved.

Keywords: plasma etching, contact-hole etching, heptafluoropropyl methyl ether, perfluorocarbon, global warming potential.

1. Introduction

During high aspect ratio contact-hole etching, high energy ions are subjected to colliding with a mask such as photoresists and amorphous carbon layers (ACLs), causing damage and corrosion to the mask. This results in various pattern deformations such as bowing, necking, and tilting [1]. As this pattern deformation causes defects in the ULSI devices and reduces the degree of circuit integration by decreasing the margin between holes, its minimization is important.

Etching of SiO₂ contact holes is mainly performed using fluorocarbon plasmas such as CF₄ and C₄F₈ plasmas. When a substrate is exposed to the fluorocarbon plasmas, a passivating fluorocarbon film is formed on the surface of the substrate [2]. The fluorocarbon film protects the mask and the sidewalls of contact holes from etching, thus enabling anisotropic profiles with high aspect ratios. Fluorocarbon gases such as CF_4 and C_4F_8 , which are widely used for etching of SiO₂ contact holes, are perfluorocarbons (PFCs) with a high global warming potential (GWP) and a long lifetime that adversely affect global warming [3]. To solve this problem, several strategies have been attempted such as process optimization, abatement [4], and recycling [5], but there is a limit to using a gas with high GWP. Therefore, an etching process using a material with a low GWP is required.

Various compounds such as unsaturated fluorocarbons [6-8], iodo-fluorocarbons [9, 10], fluorinated ethers [11–13], and fluorinated alcohols [13, 14] have been explored as lower-GWP alternatives to PFCs to develop an environmentally friendly etching process. Among them, fluorinated ethers are attracting attention because they have low GWPs and contain an oxygen atom.

In this study, SiO_2 contact holes were etched using heptafluoropropyl methyl ether (HFE-347mcc3)/O₂/Ar plasmas, and the etch profiles were investigated at various flow rates of HFE-347mcc3. The angular dependences of the deposition rate of fluorocarbon films on the surface of SiO₂ and the etch rate of SiO₂ were also investigated to explain the shape evolution of SiO_2 contact holes etched in HFE-347mcc3/O₂/Ar plasmas.

2. Experiment

SiO₂ contact-hole etching was conducted in an inductively coupled plasma (ICP) system as shown in Fig. 1. The discharge gas was a mixture of HFE- $347mcc3/O_2/Ar$. The total flow rate of HFE- $347mcc3/O_2/Ar$ was 30 sccm. The flow rate of O₂ was fixed at 2 sccm. The flow rate of HFE- $347mcc3/O_2/Ar$ was 30 sccm. The source power and the bias voltage were 250 W and -1200 V, respectively. The pressure in the ICP chamber was 1.33 Pa, and the electrode temperature was set at 15°C.



Fig. 1. Schematic diagram of an ICP system.

The shape evolution of the contact-hole etch profiles was analyzed using a patterned sample. Fig. 2 shows the cross-sectional scanning electron microscopy (SEM) images of the patterned sample. A 2400-nm-thick SiO_2 film for contact-hole etching was on a Si substrate. A 1350-nm-thick ACL with a hole diameter of 200 nm was used as a mask.

A Faraday cage system fixed to the ICP chamber electrode was used to measure the deposition rate of fluorocarbon films formed on the surface of SiO_2 and the etch rate of SiO_2 at various ion-incident angles. Here, the ion-incident angle was referred to as the angle between the ion-incident direction and the surface normal to the sample.



Fig. 2. Cross-sectional SEM images of the hole-patterned sample.

3. Results

Fig. 3 shows SEM images of SiO₂ holes etched in the HFE-347mcc3/O₂/Ar plasmas at various flow rates of HFE-347mcc3/O₂/Ar. When the flow rates of HFE-347mcc3/O₂/Ar are 8/2/20 sccm, the top diameter of the SiO₂ hole slightly decreased to 197 nm (from 200 nm before etching), and bowing of the hole was observed. Moreover, the top diameter remained constant even when the flow rate of HFE-347mcc3 was increased (HFE- $347 \text{mcc} 3/\text{O}_2/\text{Ar} = 9/2/19$ sccm). However, narrowing rather than bowing occurred, and the etch profile appeared more anisotropic than that at HFE-347mcc3/O₂/Ar = 8/2/20 sccm. As the HFE-347mcc3 flow rate further increased, the top diameter of the SiO₂ hole decreased, and the narrowing of the SiO2 hole worsened. Severe narrowing with increasing the HFE-347mcc3 flow rate eventually resulted in an etch stop at the flow rates of HFE-347mcc3 higher than 11 sccm.



Fig. 3. SEM images of 200-nm-diameter SiO_2 holes etched in the HFE-347mcc3/O₂/Ar plasmas at various flow rates for HFE-347mcc3/O₂/Ar.

4. References

[1] J. -K. Lee, I. -Y. Jang, S. -H. Lee, C. -K. Kim, and S. H. Moon, Journal of The Electrochemical Society, **157**, D142 (2010).

[2] K. Takahashi, M. Hori, M. Inayoshi, and T. Goto, Japanese Journal of Applied Physics, **35**, 3635 (1996).

[3] IPCC 6th assessment report (2021).

[4] K. Suzuki, Y. Ishihara, K. Sakoda, Y. Shirai, A. Teramoto, M. Hirayama, T. Ohimi, T. Watanabe, and T. Ito, IEEE Transaction on Semiconductor Manufacturing, **21**, 668 (2008).

[5] Y. Tajima, T. Futatsuki, T. Abe, and S. Tanzawa. IEEE Transaction on Semiconductor Manufacturing, **18**, 495 (2005).

[6] S. Kim, D. Choi, T. Hong, T. Park, D. Kim, Y. Song, and C. Kim, Journal of Vacuum Science & Technology A, **23**, 953 (2005).

[7] D. Sung, L. Wen, H. Tak, H. Lee, D. Kim, and G. Yeom, Materials, **15**, 1300 (2022).

[8] S. -W. Cho, C. -K. Kim, J. -K. Lee, S. H. Moon, and H. Chae, Journal of Vacuum Science & Technology A, **30**, 051301 (2012).

[9] S. Karecki, L. Pruette, R. Reif, T. Sparks, L. Beu, and V. Vartanian, Journal of The Electrochemical Society, **145**, 4305 (1998).

[10] S. Samukawa and K. Tsuda, Japanese Journal of Applied Physics, **37**, L1095 (1998).

[11] J. -H. Kim, J. -S. Park, and C. -K. Kim, Applied Surface Science, **508**, 144787 (2020).

[12] J. -H. Kim, J. -S. Park, and C. -K. Kim, ECS Journal of Solid State Science and Technology, 7, Q218 (2018).

[13] Y. Kim, S. Kim, H. Kang, S. You, C. Kim, and H. Chae, ACS Sustainable Chemistry & Engineering, **10**, 10537 (2022).

[14] S. You, Y. J. Lee, H. Chae, and C. -K. Kim, Coatings, **12**, 679 (2022).