Effect of UV Photons and Radicals for Low-Frequency Line-Edge Roughness (LER) of ArF Photo-resist during Fluorocarbon plasma etching

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1. Introduction
The influence of low-frequency line-edge roughness (LER) of a few tens of nm on the critical dimensions (CDs) relatively increases as the pitch size of interconnects becomes smaller than 100 nm. Low-frequency LER causes problems such as higher leakage current and time-dependent dielectric breakdown (TDBB) [1]. We investigated the roughening mechanism of ArF photoresist during etching to find out why CF₃I gas reduces the LER in the etching step of multi-layer photoresists [2]. Since the plasma of reactive ion etching (RIE) consists of ultraviolet (UV) photons, radicals, and ions, we used a UV lamp and a neutral beam source for evaluating the effect of different plasma compositions on photo-resist roughness.

2. Experimental
A capacitive coupled plasma (CCP) etching machine was used to etch patterned wafers. One hundred-nanometer pitch multi-layer photo-resists on porous SiOC were fabricated using 193-nm ArF immersion lithography. The multi-layer photo-resist consisted of ArF photo-resist, anti-reflective coating (ARC), spin-on glass (SOG), and spin-on carbon (SOC), from the top surface. We etched the SOG film using CF₃I or CF₄ gases. This CCP machine was also used to evaluate the LER formation mechanism by using non-patterned ArF resist film.

We used another type of etching machine consisting of an inductively coupled plasma source and parallel carbon plates to produce a neutral beam (NB) [3]. An NB consists of neutral atoms and radicals without ions or UV photons.

To evaluate the effect of UV photons on roughness, we used a UV lamp at 25°C. Ar was used as the inert gas.

The 180-nm-thick ArF resist films were coated and baked on a silicon wafer. We evaluated the characteristics of the photo-resists by irradiating them with the UV lamp, NB, and plasma using SEM, Fourier-transform infrared spectroscopy (FT-IR), x-ray photoelectron spectroscopy (XPS), a nanoindenter, and stress measurements.

3. Results and Discussion
First, we observed the effect of SOG-etching gases on LER for resist CDs from 45 to 80 nm (Fig. 1). The etching gases were CF₃I or CF₄ for SOG and CF₃I for porous SiOC. The LERs were estimated after porous SiOC etching and resist ashing. The initial LERs were small and constant regardless of the width of the resist CDs. The LER for the CF₃I plasma was similar to that of the initial ArF resist. On the other hand, the LER for the CF₄ plasma was larger, and it was especially greater for narrower pitches less than 50 nm. The LER for the CF₃ plasma had two frequencies (small and large roughnesses). These two frequencies were caused by the resist polymer grain (high-frequency) and wiggling (low-frequency). We focused on the low-frequency LER mechanism.

Fig. 1 LER dependence on resist CD; ●: SOG etching by CF₃I, ■: SOG etching by CF₄, ◆: initial ArF resist.

To investigate the ArF resist surface and plasma reactions, we evaluated the properties of the resist films after exposure to the UV lamp, NB, and CCP. First, we observed

Fig. 2 Tilt SEM images in ArF resist films irradiated by UV ramp, neutral beam and CCP without bias; (a) initial, (b) UV 0.5min, (c) NB CF₃I 10min, (d) NB CF₄ 10min, (e) CCP CF₃I 1min, (f) CCP CF₄ 1min.
the SEM images of ArF resist films treated with these processes (Fig. 2). The surface roughness was small with the UV lamp and NB for both CF$_3$I and CF$_4$. On the other hand, an undulation appeared with CCP. The modified layer formed in the CF$_2$ plasma at the surface of the film seems to be thicker than the one formed in the CF$_3$I plasma. The undulations on the film are thought related to the wiggling of the patterned resist.

We analyzed the films after exposure to the UV lamp using FTIR. The FTIR spectra revealed that the C=O bonds in the ester deteriorated due to UV photons.

We also analyzed the depth profiles of fluorine, carbon, oxygen, and iodine of the UV lamp-, NB- and CCP- irradiated ArF resist surface using XPS (Fig. 3). The oxygen concentration for the UV-lamp sample decreased up to a depth of 170 nm compared with the initial conditions (Fig. 3(b)). Since the ester disappeared in the C1s peak up to a depth of 170 nm, the film surface must have absorbed UV photons. The XPS data of the CCP sample indicated that the oxygen concentration decreased up to a depth of 40 nm for CF$_3$I and 80 nm for CF$_4$ compared with the initial conditions (Fig. 3(e), (f)). Besides the UV-lamp results, the C=O bonds in esters were degraded due to UV photons in the plasma. We assumed that the C=O degradation was affected by the UV intensity of the plasma because the UV intensity of the CF$_3$I plasma was smaller than that of the CF$_2$ plasma. Moreover, both CF$_3$I and CF$_4$ plasmas caused fluorine atoms to accumulate near the top surface. The C1s peak from XPS of the surface indicated that the ester was degraded; therefore, CF and CF$_2$ appeared in both plasmas. We assumed that the concentration of surface fluorine was affected by the amount of fluorine radicals in the plasma because CF$_3$I had few F radicals. These results indicate that UV photons in the plasma degraded the C=O bonds, and F radicals attached to the dangling bonds. The region with the change in carbon concentration seems to be the same as the one with the change in fluorine concentration. This region coincided with the thickness of the surface-modified layer. The modified layer subjected to CF$_3$I plasma was thinner than the one subjected to CF$_4$ plasma.

In the NB sample, the regions with the oxygen and fluorine concentration changes were small (Fig. 3 (c), (d)). This is because there are few UV photons and fluorine radicals in an NB.

We also evaluated the wafer stress of the plasma-irradiated film to investigate the correlation between the surface-modified layer and wiggling. Although stress did not change in the CF$_3$I plasma, it increased in the CF$_4$ plasma. This indicates that the CF modified-layer shrunk.

4. Conclusions

We clarified the mechanism of low frequency LER formation in ArF photo-resist patterns during plasma etching using fluorocarbon gases. The C=O bonds in the ArF resist polymer were broken by UV photons, and F radicals subsequently formed a CF-modified layer at the surface. This surface modification led to resist roughness due to the stress between the shrunken surface layer and inner bulk resist. We conclude that CF$_3$I gas with a lower UV intensity and fewer F radicals is better at suppressing wiggling in CCP. In addition, an NB using CF$_3$I gas might be able to suppress wiggling by minimizing the CF-modified layer in the CF$_4$ plasma.

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References

