Silicon Infiltration into Functional Polymer for Nanoscale Pattern Development

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We report on the utility of self-aligned quadruple patterning (SAQP) using dual carbon layers as mandrels and silicon oxide films as spacers to improve pattern comprehensive pattern fidelity, such as line edge roughness (LER)/line width roughness, local critical dimension uniformity, and pattern placement, compared to the design. While the use of carbon layers and silicon oxide films enables reduced LER, the required etching selectivity between the two carbon layers was difficult to obtain. We gained this selectivity by infiltrating silicon into one carbon layer. Thus, a SAQP scheme was developed and successfully demonstrated to produce a sub-20-nm half pitch pattern. The low LER value obtained after etching the first carbon layer was preserved throughout the process.

Keywords: Dual-carbon, Infiltration, Self-aligned quadruple patterning

1. Introduction

The continued scaling of the minimum feature sizes in integrated circuits not only requires novel device designs but also the development of photolithography. Extreme ultraviolet (EUV) lithography with an exposure wavelength of 13.5 nm is considered to be a promising alternative for lithography and has made excellent progress over the past few years [1-4]. Prior to implementation of EUV lithography for high volume manufacturing, however, extension of ArF immersion lithography by multiple-patterning is required as a complementary approach [5-8]. Self-aligned patterning, a spacer defined process, is already applied to the mass-production because it can easily make high resolution patterns based on repetition of simple processes. In order to develop more complicated patterns and enhance the pattern fidelity for future applications, however, spacer-related patterning techniques need to improve both line edge roughness (LER) and pitch-walk.

A final pattern roughness improvement could be achieved by reduction of the mandrels’ LER and by preservation of this low LER during pattern development. Therefore, the mandrels and spacers have to be carefully selected because the core space, the gap space, and the spacer-defined space will originate from these components in self-aligned quadruple patterning (SAQP). In the conventional SAQP process, amorphous silicon and carbon are stacked as the first and second mandrel, respectively; silicon oxide is deposited as both the first and the second spacer. While the etch selectivity of carbon versus silicon oxide is high, that of silicon versus silicon oxide is relatively low, and is a potential contributor to LER. On the other hand, line width roughness will be minimized and remain constant because atomic layer deposition (ALD) has high thickness controllability and conformality through spacer fabrication. We believe
that SAQP with dual carbon mandrels and dual silicon oxide spacers enables more complicated patterns [9] and have thus launched a SAQP scheme having a dual carbon stack (Fig. 1). In addition, this scheme mitigates some SAQP process complexity and improves its affordability, since the stacking layers are spin-on materials.

To realize this proposed SAQP scheme, we faced two challenges with etch selectivity: one is between two carbon layers, and the other between a carbon layer and silicon oxide. To overcome these challenges, we examined trimethylsilyldimethylamine (TMSDMA) infiltration into a functional polymer to generate an etch-selective carbon layer. In this letter, we report the properties of this silicon containing polymer and the achievement of sub-20-nm half pitch (hp) pattern development by dual carbon stack SAQP, having reduced LER after the first carbon mandrel removal.

2. Experimental

2.1. Materials

Two types of functional polymers were supplied from Tokyo Ohka Kogyo Co., Ltd. One is an acrylic polymer, and the other is a phenolic polymer. The substrates used for this work were 200 mm Si wafers.

2.2. Silicon infiltration process

Alternative exposures of TMSDMA and H$_2$O vapor were repeated to infiltrate silicon content into the polymers. A schematic of the TMSDMA infiltration process is shown in Fig. 2. After transferring the substrate into the chamber, air was evacuated and the temperature was set at 100, 125, 150, and 175ºC, respectively. The infiltration was initiated by introducing TMSDMA through the vaporizer line. The pressure was maintained at 2000 Pa for 15 min. Then, N$_2$ as an inert gas was used to purge the chamber and to remove excess reactants. A similar process of H$_2$O/N$_2$ was carried out to complete the infiltration. The altered polymers were characterized by Fourier transform infrared spectroscopy (FTIR), time of flight secondary ion mass spectroscopy (ToF-SIMS), x-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Ar gas cluster ion beam with an acceleration voltage of 1 kV and Ar ion sputtering with 3 kV were employed for ToF-SIMS and XPS depth profiling, respectively.

2.3. Etch durability

Reactive ion etching (RIE) with the following gases were carried out in a plasma etching module: O$_2$/N$_2$, H$_2$/N$_2$, CF$_4$, Cl$_2$, and HBr. The polymer coated substrates were also immersed in a 0.5% diluted hydrofluoric acid (dHF) aqueous solution or propyleneglycol monomethyl ether acetate (PGMEA) for wet-etch testing. Etch rates were calculated from the loss of film thicknesses, which were measured by ellipsometry.
2.4. Development of SAQP

After the functional polymers were deposited on the silicon substrates by the spin coating, TMSDMA infiltration was performed to alter their properties. Spin-on-carbon (SOC), silicon antireflective coating (SiARC), bottom antireflective coating, and ArF photoresist (PR) were stacked in the listed order. A 75 nm hp PR pattern was fabricated using 193 nm exposure. Self-aligned quadruple patterning was carried out with following steps: SOC mandrel etch, first silicon oxide spacer deposition, silicon infiltrated polymer etch, second silicon oxide spacer deposition with ALD, and finally, pattern transfer to silicon pitch-divided spacer pattern by RIE. Critical dimension (CD) and LER measurements and an SEM image were obtained after each process.

3. Results and discussion

3.1. Evaluation of silicon-infiltrated polymer

Figure 3(a) shows the XPS depth profiles of the acrylic polymer after silicon infiltration at 100ºC. Spectrum measurements were carried out after the films were etched 10, 20 and 30 nm, respectively. The etched film thickness was derived from the time required to etch the entire film. The surface of the acrylic polymer shows two peaks in the Si $2p$ region of the spectrum. These were identified as being due to Si-C and Si-O bonding, respectively. The Si $2p$ peak diminished as the film was etched and finally, at a depth ~30 nm, the peak vanished. On the other hand, the peak intensity 30 nm deep in the phenolic polymer has almost the same peak intensity at the surface, as shown in Fig. 3(b). These results indicate that TMSDMA is better able to infiltrate into phenolic polymer than in acrylic polymer. This observation might be due to the steric hindrance of the functional groups, e.g., the adamantyl and lactone group in the latter polymer that could hinder diffusion.

For further analyses, we measured attenuated total reflectance FT-IR spectroscopy (Fig. 4). The spectrum of acrylic polymer remained effectively unchanged after TMSDMA exposure while 3 new features (green lines in the figure) appeared in the phenolic polymer’s spectrum as shown in Fig. 4. Absorbances at 845 and 1250 cm$^{-1}$ are assigned to Si-(CH$_3$)$_3$ modes while that at 917 cm$^{-1}$ is expected to be due to TMSDMA chemisorption.
As those peaks appeared, the O-H stretching band at ~3600 cm$^{-1}$ decreased. Meanwhile, the peak at 1500 cm$^{-1}$, which is characteristic of aromatic C=C bonds, maintained the same intensity. These results suggest that TMSDMA molecules chemisorbed in the phenolic polymer as the trimethylsiloxyl group.

To calculate the maximum silicon concentration and to reveal the depth that TMSDMA infiltrated, we examined TMSDMA exposure at 2000 Pa at various temperatures. The film thickness of the phenolic polymer was maintained at 60 nm. From the XPS measurement, the atomic concentration of silicon in the polymer was calculated to be ~8% regardless of the temperature. This result indicates that the maximum concentration of silicon is constant and independent of the TMSDMA exposure temperature. The depth profiles of trimethylsilyl group (C$_3$H$_9$Si) ion intensities were measured by ToF-SIMS as shown in Fig. 5. The normalized film thickness was derived from the depth profile of silicon ion. The ion intensities near the surface were constant, which agrees well with the XPS measurement. When the TMSDMA was exposed at 100ºC, TMSDMA infiltrated through only about one-third of the film thickness, to a depth of ~20 nm. At temperatures above 125ºC, however, nearly the entire film had reacted with TMSDMA as evidenced by a nearly constant trimethysilyl group concentration throughout.

### 3.2. The etch selectivity of altered polymer

We summarize the various etch rates of as-deposited and silicon-contained phenolic polymer, SOC and silicon oxide in Table 1. The durability of the polymer to O$_2$-RIE was significantly improved by TMSDMA infiltration since a thin SiO$_2$ layer was formed on carbon surface. This indicates we have dealt with one of the challenges which is etch selectivity between two carbon layers. Durability to H$_2$-RIE also improved because silicon is also less likely to be etched under these conditions. On the other hand, the etch rates of CF$_4$-, CH$_2$F$_2$-, Cl$_2$- and HBr-RIE all increased. We believe trimethylsilyl group makes the film susceptible to halogen species that promote etching. These etching results led us to use H$_2$-RIE for the second carbon mandrel etch because it obtained the desired high etch selectivity to silicon oxide. On the other hand, the durability of polymer to dHF and PGMEA did not change at all by TMSDMA infiltration. A unique phenomenon here is that the functional polymer gains metal-like properties by the infiltration of TMSDMA functionally, even though as noted above, the silicon atomic concentration was less than 10%.

### 3.3. Demonstration of SAQP

We demonstrated SAQP based on the scheme in Fig. 2. Top-view SEM images with the values of CD and LER at each process are shown in Fig. 6. Using this scheme, we have successfully achieved SAQP with a resolution of sub-20–nm hp. We confirmed that the pattern was developed only when the polymer used as the second mandrel had been infiltrated with TMSDMA. Another achievement of this process is that a LER was fixed after the SOC mandrel etch. This means that the line-edge roughness was transferred unchanged to the spacers and to the second mandrel. The value of LER was preserved throughout the SAQP process because we employed carbon films for both mandrels and obtained high etching selectivity between the spacers and mandrels.

![Fig. 5. C$_3$H$_9$Si ion depth profile of phenolic polymers for as-deposited and TMSDMA exposed at various temperatures.](image_url)
4. Conclusion

We have studied the properties of the phenolic polymer with TMSDMA infiltration and demonstrated a self-aligned quadruple patterning scheme with dual-carbon stack. By infiltrating TMSDMA, etch selectivity between two carbon layers was obtained. We successfully fabricated a sub-20-nm hp pattern which maintained the same line edge roughness of the first carbon mandrel. These results indicate that the dual-carbon stack scheme is a practical solution for improving pattern fidelity, mitigating process complexity and increasing affordability.

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