Photosensitive porous low-k interlayer dielectric film

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1. Introduction
The increase of interconnect RC-delay has occurred as the reverse effect due to the scaling down of the ultra-large-scale-integrated circuits (ULSI). Therefore, the interconnect technologies with low-resistance metal wire and low-k interlayer film are needed for ULSI. Methylsilsesquioxane (MSQ) is one of the low-k films. Methylsilsesquiazane (MSZ) is a precursor component of MSQ. When a photo-acid generator (PAG) molecule is added to MSZ, it acquires the photosensitivity. Lithography of photosensitive MSQ was examined by using UV light, KrF excimer laser, electron beam and SOR X-ray [1-5]. For the reduction of dielectric constant, a photosensitive porous MSQ low-k film was developed [4]. And also analysis of patterning profile on photosensitive MSZ was discussed [5]. Photosensitive MSZ enable us to eliminate the resist coating, dryetching and ashing in the ULSI interconnect fabrication process, and so that process step can be reduced. In this paper the effect of electron-beam dose, humidification and development process on the critical dimension of photosensitive MSZ is discussed.

2. Experimental
Photosensitive MSZ precursor was spin-coated to the thickness of 400 nm on 2 inch Si(100) wafers at 2000 rpm for 20 sec. It was prebaked at 110 °C for 1 minute. The electron-beam lithography was performed by use of Hitachi HL-700 electron-beam stepper. The electron-beam energy was 50 keV. After electron-beam exposure, the wafer was placed in the humid environment (23 °C, 50 %RH) for 15, 30 and 60 minutes. The electron-beam exposed MSZ films were developed in 2.38 %tetra-methyl-ammonium-hydride (TMAH) aqueous solution for 90 seconds. In the development the wafer was bathed in TMAH aqueous solution with an ultrasonic cleaner. Then the wafer was rinsed in deionised water for 2 minutes, and was spin-dried.

3. Results and Discussion
Lithographic characteristics of photosensitive MSZ are dependent on electron beam exposure dose and humidification treatment. Figure 3 shows humidification time dependence of critical exposure dose. Figure 3 shows that longer humidification treatment resulted in the lower critical exposure dose, e.g., in the 100 nm design line and space pattern, the critical exposure dose was 80 µC/cm² in 15 min humidification treatment process, while 35 µC/cm² for 60 min humidification treatment process. Figure 4 shows the SEM micrographs before and after the critical exposure dose. It is found that as the humidification treatment became long, the exposure width was enlarged. Figure 5 shows the relation between feature size and exposure dose for humidification processes. As the humidification time became long, slope of the curves became steep. The feature size at the critical exposure dose was larger than the design size. The feature sizes have a linear correlation with exposure dose as shown in Fig. 5, it is expected that the reduction of the critical exposure dose minimize the feature sizes. To improve critical exposure dose, the development with ultrasonic wave was carried out. Figure 6 shows that the SEM micrographs of photosensitive MSZ after the development with or without ultrasonic wave. Insufficient developed patterns at the non-ultrasonic development were cleaned up at the ultrasonic development. The critical exposure dose shifted from 80 µC/cm² to 65 µC/cm² as shown in Fig. 7.

4. Conclusion
Characteristics of photosensitive MSZ-MSQ low-k film were investigated using electron-beam lithography. The relationship between electron-beam exposure dose and humidification was discussed. Longer humidification time made the critical exposure dose lower, however the feature sizes were enlarged. The critical exposure dose for 100 nm line and space pattern were 80 µC/cm², 45 µC/cm² and 30 µC/cm² for humidification times of 15 min, 30 min and 60 min, respectively. The ultrasonic development was carried out to reduce the critical exposure from 80 µC/cm² to 65 µC/cm².

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References
Chemical Amplified Effect

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Chemical Amplified Effect

N
N
H
N
H

photosensitive MSZ by electron-beam exposure and H2O adsorption.

Fig. 2. Schematic diagram of chemical amplified mechanism of photosensitive MSZ by electron-beam exposure and H2O adsorption.

Base polymer: MSZ

Fig. 3. Critical exposure dose for photosensitive MSZ: measurements were performed at 50, 75 and 100 nm design size line and space patterns. Feature sizes are normalized by each design size.

(a) MSZ: Methylsilsesquiazane  (b) MSQ: Methylsilsesquioxane

Fig. 1. The chemical structure of methylsilsesquiazane (MSZ) and methylsilsesquioxane (MSQ). After the humidification treatment and annealing at 400 °C, MSZ is changed into MSQ.

Spin-Coating  Electron-beam Exposure  Humidification  Chemical Amplified Effect

Photocid generator: TAZ-104 (Midori Kagaku)

Fig. 6. SEM micrographs of photosensitive MSZ for the development with or without ultrasonic wave. (Humidification treatment: 23 °C, 50 %RH, 15 min)

Fig. 5. Measured feature size versus electron-beam dose for photosensitive MSZ: measurements were performed at 50, 75 and 100 nm design size line and space patterns. Feature sizes are normalized by each design size.

<table>
<thead>
<tr>
<th>Without ultrasonic wave</th>
<th>With ultrasonic wave</th>
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<tbody>
<tr>
<td><strong>Dose:</strong> 65 µC/cm²</td>
<td>75 µC/cm²</td>
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<tr>
<td>Design Size: 100 nm</td>
<td>200 nm</td>
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<td>75 nm</td>
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<td>100 nm</td>
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Fig. 4. SEM micrographs of photosensitive MSZ in 15 min, 30 min and 60 min humidification process (23 °C, 50 %RH). These are micrographs before and after critical exposure dose.

Fig. 7. Normalized feature size for 100 nm design size line and space patterns. Ultrasonic development reduces the critical exposure dose.
Advantage of Photosensitive Low-κ

**Material & Film Formation**

Photosensitive MSQ

Chemical Amplified Resists

400℃ Curing

Si-O-Si

CH3

CH3

Si-N-Si

MSQ: Methylsilsesquioxane

Process Flow

Electron-Beam Lithography

Without ultrasonic wave

With ultrasonic wave

Improvement of Pattern Shape

Critical Exposure Dose & Humidification Time

Summary

1. Characteristics of photosensitive MSZ-MSQ low-k film were investigated using electron-beam lithography.
2. Pattern shape was improved. The process with higher hydrogen concentration and lower water concentration inside the pattern shape improved.
3. The relationship between electron-beam exposure dose and humidification was discussed. Longer humidification time made the critical exposure dose lower, however, the feature sizes were enlarged. The critical exposure dose for 100 nm line and space pattern were 80 µC/cm² for 85 µC/cm² and 55 µC/cm² for the humidification times of 15 min, 30 min, and 60 min, respectively.
4. Controllability of pattern width was improved: the ultrasonic development was carried out to reduce the critical exposure from 80 µC/cm² to 65 µC/cm².

Summary