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 $\mu C/cm^2$ in 15 min humidification treatment process, while 35 $\mu C/cm^2$ 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 $\mu C/cm^2$ to 65 $\mu C/cm^2$ 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 $\mu C/cm^2$, 45 $\mu C/cm^2$ and 30 $\mu C/cm^2$ 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 $\mu C/cm^2$ to 65 $\mu C/cm^2$.

Acknowledgment

Part of this work was supported by NEDO under the management of ASET in METI's R&D.

References

[1]. T. Kikkawa, T. Nagahara and H.Matsuo, Appl. Phys. Lett., **78**, 2557 (2001).
[2]. M. Tada, T. Ogura, and Y. Hayashi, Ext. Abst. the 2002 Int. Conf. Solid State Devices and Materials, 44, Business Center for Academic Societies Japan, Tokyo (2002).
[3]. S. Kuroki, T. Kikkawa, H. Kochiya and S. Shishiguchi, Jpn. J. Appl. Phys., **42**, 1907 (2003)
[4]. S. Kuroki, S. Sakamoto and T. Kikkawa, *Jpn. J. Appl. Phys.*, **43**, 1820 (2004).
[5]. S. Kuroki and T. Kikkawa, J. Electrochem. Soc., (to be published).

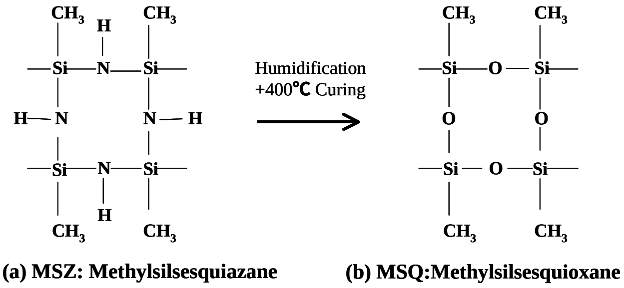

Fig. 1.The chemical structure of methylsilsesquiazane (MSZ) and methylsilsesquioxane (MSQ). After the humidification treatment and annealing at 400 ℃, MSZ is changed into MSQ.

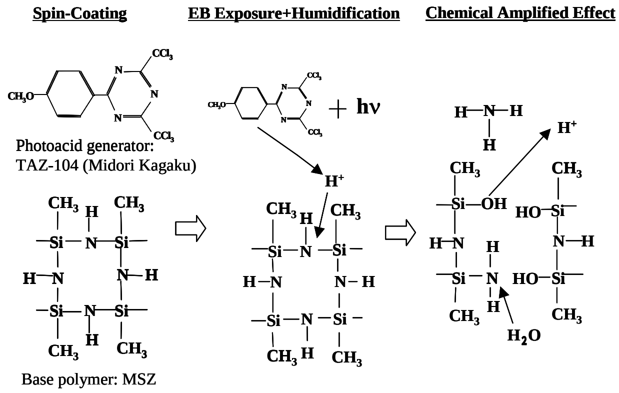

Fig. 2. Schematic diagram of chemical amplified mechanism of photosensitive MSZ by electron-beam exposure and H_2O adsorption.

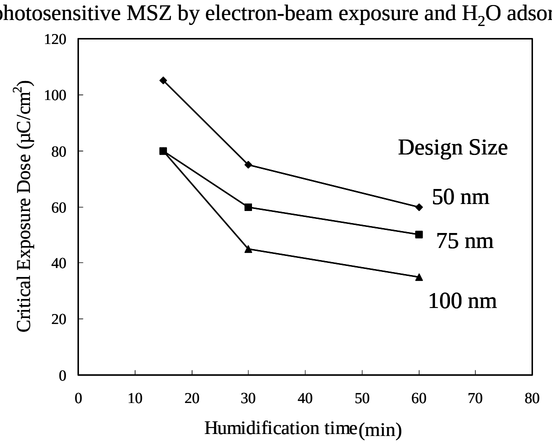

Fig. 3. Critical exposure dose for photosensitive MSZ.: measurements were performed at the 50, 75 and 100 nm design size line and space patterns.

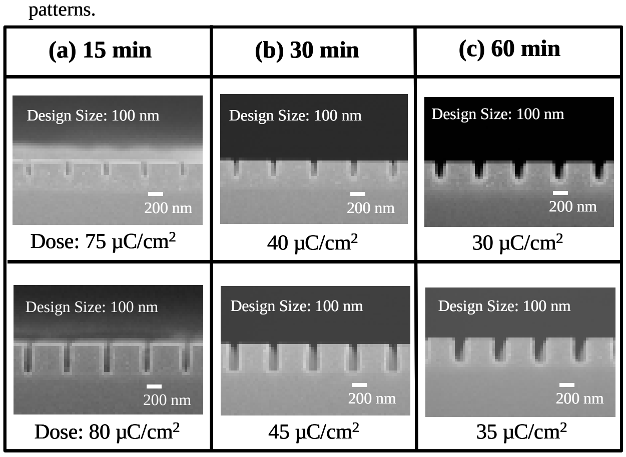

Fig. 4. SEM micrographs of photosensitive MSZ in 15 min, 30 min and 60 min humidification process (23 ℃, 50 %RH). These are micrographs before and after critical exposure dose.

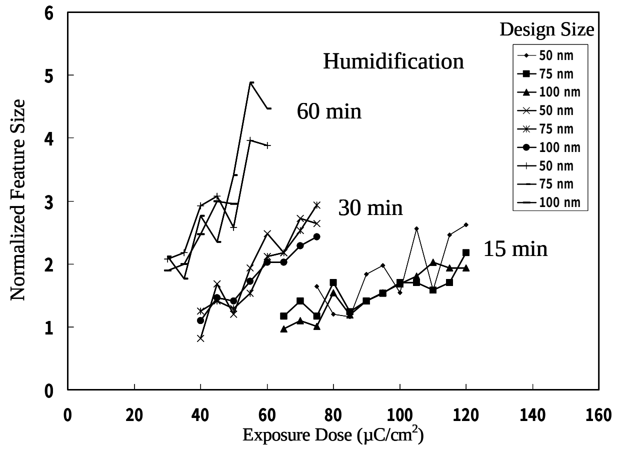

Fig. 5. Measured feature size versus electron-beam dose for photosensitive MSZ: measurements were performed at 50, 75 and 100 nm design size line and space patterns. Feature sizes are normalized by each design size.

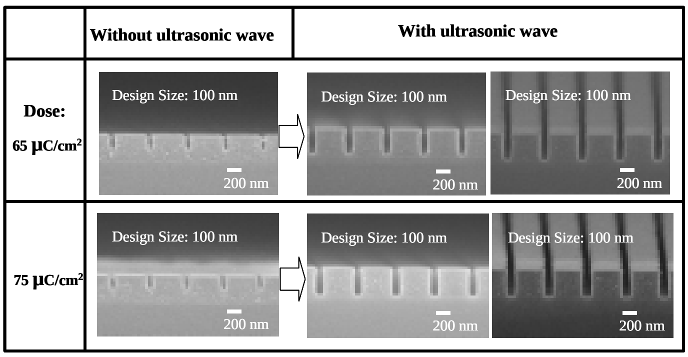

Fig. 6. SEM micrographs of photosensitive MSZ for the development with or without ultrasonic wave. (Humidification treatment: 23 °C, 50 %RH, 15 min)

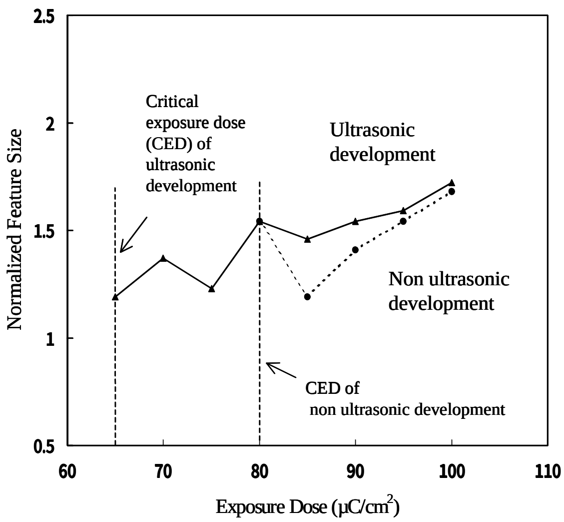

Fig. 7. Normalized feature size for 100 nm design size line and space patterns.Ultrasonic development reduces the critical exposure dose.

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Advantage of Photosensitive Low-k

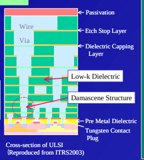
ULSI interconnect integration with low-k interlayer dielectric film

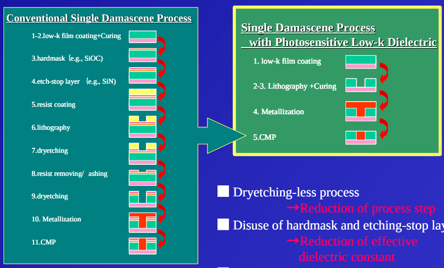
Problem of damascene fabrication: lowering of low-k reliability by dryetching and ashing.

Dryetching-less process

PURPOSE

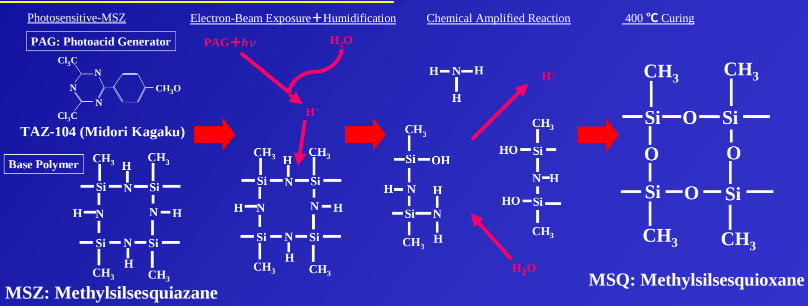
DEVELOPMENT of Photosensitive Low-k Dielectrics



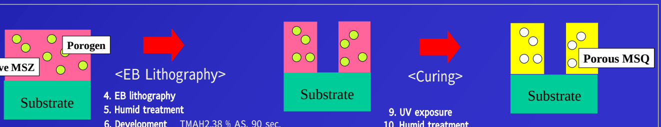


- Dryetching-less process
  →Reduction of process step
- Disuse of hardmask and etching-stop layer
  →Reduction of effective dielectric constant
- Solution to dryetching problem

Material & Film Formation



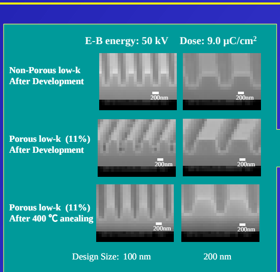
Process Flow



<Spin-coating>

1. Baking 200 ℃, 3 min.
2. Spin-coating 2000 rpm.
3. Pre-baking 110 ℃, 1 min.
4. EB lithography
5. Humid treatment
6. Development TMAH2.38 % AS, 90 sec.
7. Rinse 2 min.
8. Spin-dry 2000 rpm, 4 min.
9. UV exposure
10. Humid treatment
11. Post-baking 200 ℃, 3 min.
12. Curing 400 ℃, 30 min.

Electron-Beam Lithography



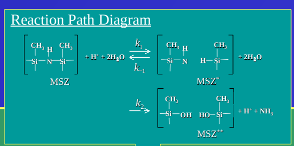
√ Patterning ➡ O. K

╳ Shape ➡ Tapered

╳ Controllability ➡ Spread

The patterning of photosensitive low-k is well performed.
However the shape of trench patterns was tapered, and the feature size was spread.
The problem is how we improve the shape and controllability of exposed patterns.

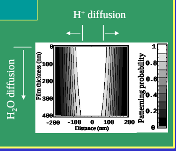
Patterning Probability



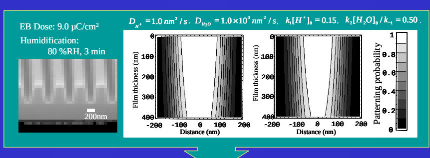
Patterning Probability

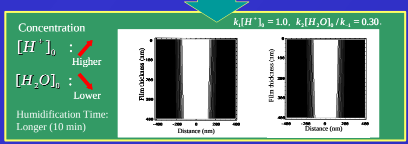
$$P(x,y,t) = \frac{[MSZ^{**}]}{[MSZ]_0} = 1 - \exp(-\gamma(x,y,t)t)$$

$$\gamma(x,y,t) = \left(1 - \frac{k_{-1}}{k_{-1} + k_2[H_2O](y,t)}\right) k_1 [H^+](x, t+\Delta t)$$



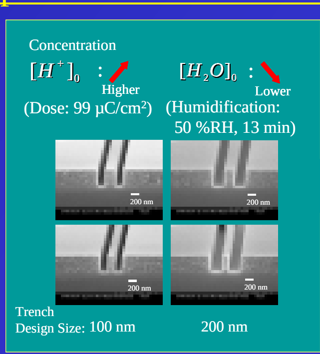
The patterning probability was defined and calculated by use of the rate reaction path in MSZ-MSQ system. A parameter gamma depend on rate constants and the density of hydrogen ion and water. From this equation the patterning probability profile was given.





Upper two figures show the patterning probability map for a conventional process. This pattern profile shows tapered shape. For an improvement of pattern shape, it is found that the higher hydrogen concentration and lower water concentration makes pattern profile abrupt. Then we applied this condition to the fabrication process.

Improvement of Pattern Shape



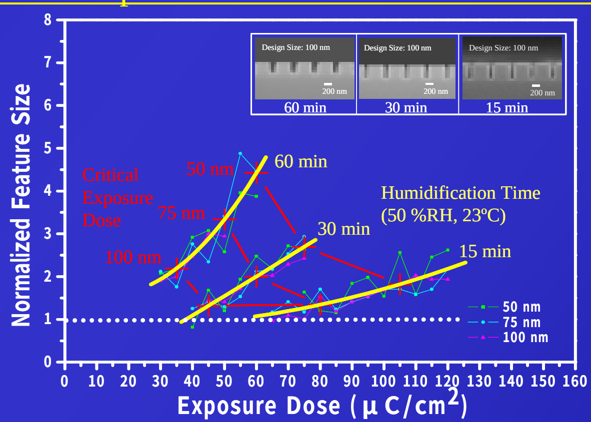
√ Patterning ➡ O. K

√ Shape ➡ O. K

╳ Controllability ➡ Spread

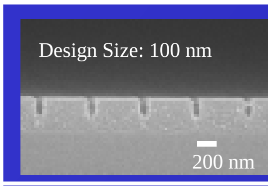
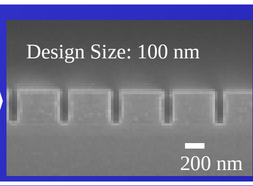
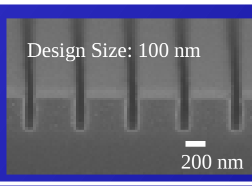
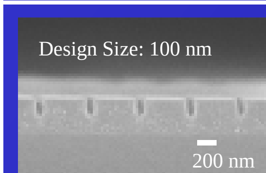
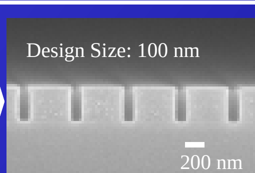
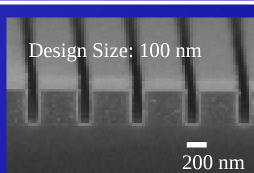
This is the results of higher hydrogen concentration and lower water concentration. The left hand side is micrographs for 100 nm trench design size, and the right hand side is micrographs for 200 nm. It is found that abrupt pattern shape was formed. Then the pattern shape was improved, however problem of the feature size controllability is not solved.

Critical Exposure Dose & Humidification Time



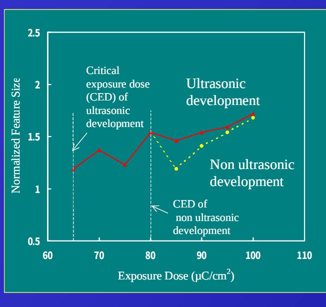
It is found that 15 min humidification time process is near to one normalized feature size. The feature sizes at the critical exposure dose was larger than the design size. Therefore, it is necessarily to reduce the feature size in the critical exposure dose. Since the feature sizes have approximately a linear correlation with exposure dose, and then 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.

Ultrasonic Development

	Without ultrasonic wave	With ultrasonic wave	
Dose: 65 μC/cm²			
75 μC/cm²			

(Each micrograph: Design Size: 100 nm; scale bar 200 nm)

Left hand side is SEM micrographs of photosensitive MSZ for development without ultrasonic wave. And right hand side is SEM micrographs of photosensitive MSZ for development with ultrasonic wave. Insufficient developed patterns at the non-ultrasonic development were cleaned up at the ultrasonic development.



Dotted line shows the non-ultrasonic development, and red line shows ultrasonic development. The critical exposure dose shifted from 80 μC/cm2 to 65 μC/cm2. And then the measured feature size for 100 nm pattern at the critical exposure dose shifted from 150 nm to 120 nm. Finally an improvement of controllability was carried out.

√ Patterning ➡ O. K

√ Shape ➡ O. K

√ Controllability ➡ Improved

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 made the pattern shape abrupt.
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, 45 μC/cm² and 30 μC/cm² for 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.

21st Century COE the 3rd Int. Workshop
December 6, 2004. Hiroshima, JAPAN