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A Novel Photosensitive Porous Low-k Interlayer Dielectric Film

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1. Introduction

In order to overcome the interconnect delay due to parasitic capacitance, porous low-k dielectrics have been introduced. It is necessary to reduce the total process cost so that photosensitive porous low-k dielectric films should be developed. Feasibility study of photosensitive non-porous low-k methylsilsesquioxane (MSQ) were carried out by using ultra-violet, KrF excimer laser, electron beam and SOR X-ray lithographies [1-3]. In this paper, a novel photosensitive porous MSQ film was developed and its characteristics were investigated.

2. Experimental

A photoacid generator (PAG) molecule is added to methylsilsesquiazane (MSZ) as a photosensitive precursor. Electron-beam lithography of photosensitive porous MSZ films was performed by use of triazine radical TAZ-104 PAG (Midori Kagaku) as shown in Fig.1. Several concentrations (0 wt%, 10 wt%, 20 wt%) of porogen were added to the photosensitive MSZ precursor. Photosensitive porous MSZ was spin-coated on 2-inch Si (100) wafers at 2000 rpm for 20 sec. It was pre-baked at 110 ℃ for 1 min. The electron-beam lithography was performed by use of Hitachi HL-700 EB stepper at 50 keV. After electron beam exposure, the wafer was placed in the humid environment (25 ℃, 80 % relative humidity, RH) for 3 min. It was developed in 2.38 % tetrakis-methyl-ammonium-hydride (TMAH) aqueous solution for 1 min. Then, the wafer was rinsed in deionised water for 2 min and spin-dried. Lithographic characteristics were analyzed by scanning electron-beam microscopy (SEM). Photosensitive porous MSZ film was exposed to ultra-violet light, and in the humid environment (25 ℃, 80 %RH) for 3 min, then post-baked at 200 ℃ for 3 min and cured at 400 ℃ for 30 min. Changes in the film composition were observed by use of FTIR spectroscopy.

3. Results and Discussion

The FTIR spectroscopy spectra of photosensitive porous MSQ are shown in Fig.2. Si-NH peaks (3413, 1172, 943 cm^{-1}) and porogen peak (1733 cm^{-1}) disappeared, and Si-O peaks (1107, 1024 cm^{-1}) appeared so that Si-O bonds replaced the Si-NH bonds. The refractive indices for photosensitive MSQ without porogen, with 10 wt% porogen and with 20 wt% porogen, measured by spectroscopic ellipsometry, were 1.377, 1.333 and 1.306, respectively. Corresponding porosities of the films were calculated from each refractive index by use of Lorentz-Lorenz equation [4]:

$$x = 1 - ((n_p^2 - 1)/(n_p^2 + 2))/((n_s^2 - 1)/(n_s^2 + 2)), \qquad (1)$$

where x is porosity, and n_p and n_s are the refractive indices of porous film and its skeleton. The result of calculation is shown in Fig. 3. Photosensitive porous MSQ (20 wt% porogen) had 17 % porosity. Pore size distributions were measured by X-ray scattering by use of Rigaku ATX-E X-ray diffractometer as shown in Fig. 4. Average pore size of photosensitive porous MSQ (20 wt% porogen) was 2.2 nm. The dielectric constant of photosensitive MSQ decreased with increasing porogen concentration as shown in Fig. 5. The dielectric constant of photosensitive porous MSQ (20 wt% porogen) was 2.62. Lithographic characteristics of photosensitive MSQ with and without porogen are shown in Figs. 6 and 7, respectively. Although porogen additive decreased the photosensitivity, the 50-200 nm line and space patterns were successfully formed. SEM micrographs of photosensitive MSQ with and without porogen are shown in Fig. 8. Porogen residues which can be evaporated at 400 ℃ cure process were observed by SEM after development. 75 nm line and space patterns in the porous MSQ film were formed by EB lithography without dryetching.

4. Conclusion

A novel photosensitive porous MSQ interlayer dielectric film was developed. Photosensitive porous MSQ (20 wt% porogen) had porosity 17 % and pore radius of 2.2 nm, and dielectric constant of 2.62. Characteristics of photosensitive porous MSQ film were investigated, and the 50-200 nm photosensitive porous MSQ patterns could be formed successfully by the electron-beam lithography without dryetching.

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References

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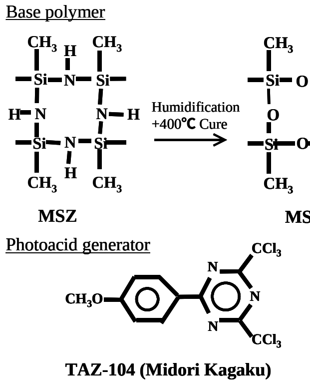


Fig. 1. Schematic diagrams of MSZ and MSQ, and photoacid generator.

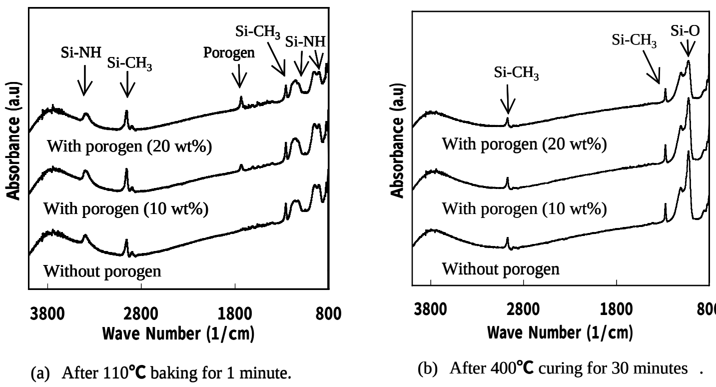


Fig. 2. FTIR spectra for photosensitive porous MSQ: (a) after pre-baking at 110 ℃ for 1 minutes, and (b) after curing at 400 ℃ for 30 minutes .

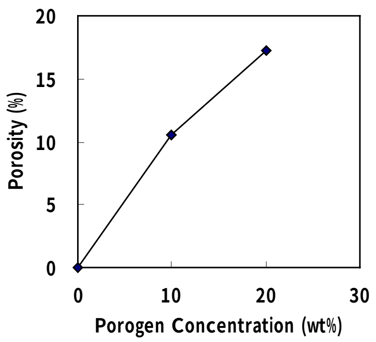


Fig. 3. Calculated porosity versus porogen concentration from measured refractive index.

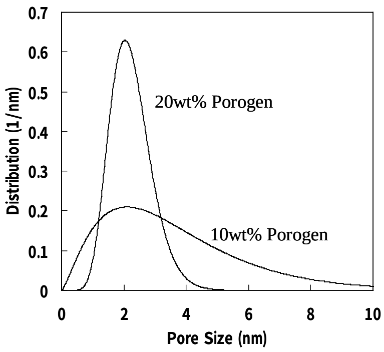


Fig. 4. Pore size distribution measured by X-ray scattering measurement.

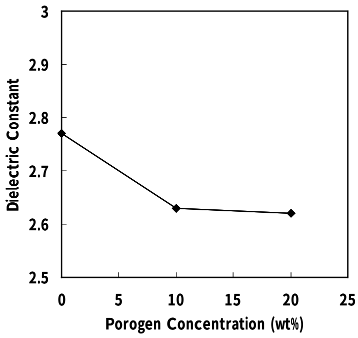


Fig. 5. Dielectric constants versus porogen concentration for photosensitive porous MSQ.

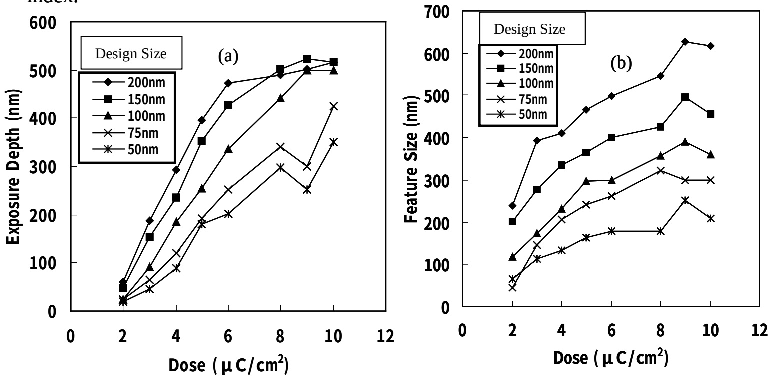
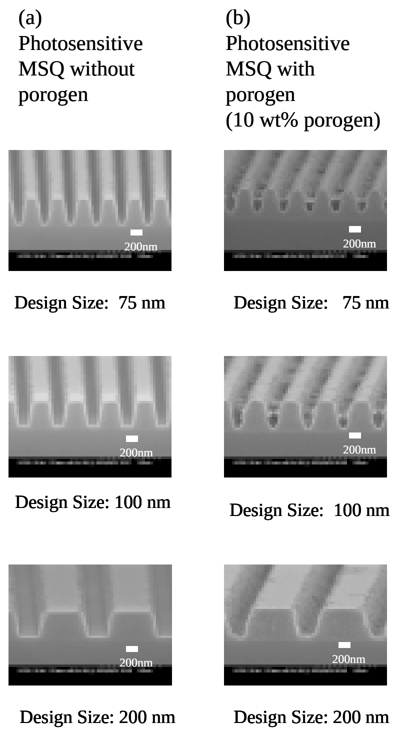


Fig. 6. Characteristic curves for photosensitive porous MSQ (10 wt% porogen) in electron-beam lithography: (a) exposure depth versus exposure dose, (b) feature size versus exposure dose.



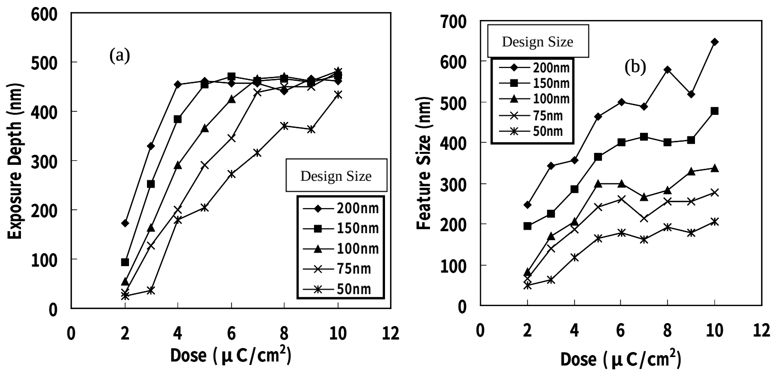


Fig. 7. Characteristic curves for photosensitive MSQ without porogen in electron-beam lithography: (a) exposure depth versus exposure dose, (b) feature size versus exposure dose.

Fig. 8. SEM micrographs of photosensitive MSQ without porogen (a) (left hand side) and with 10 wt% porogen (b) (right hand side) : (electron-beam exposure dose : 9.0 μC/cm^2, L/S=1:5)