

Preparation and Characterization of Low Dielectric Methyl Silsesquioxane (MSSQ) Thin Films

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As feature sizes in integrated circuits approach $0.18 \mu\text{m}$ and below, problems such as interconnect RC delay and crosstalk become more serious. Materials with low dielectric constants are needed to solve these problems. We applied methyl silsesquioxane (MSSQ) as a low dielectric material and studied the film formation condition and the electrical properties of MSSQ films. MSSQ dissolved in a propylene glycol methyl ether acetate (PGMEA) and MSSQ/PGMEA solution was spun on glass substrates at various concentrations. Spinning at 2,500 rpm for 30 sec resulted in films with thicknesses of $6,500 \text{ \AA}$. Then, we cured the films by heating and measured the electrical properties of samples sandwiched between Al electrodes. The dielectric constant was ~ 2.7 , the breakdown strength was about 2.3 MV/cm , and the leakage current was $5.4 \times 10^{-10} \text{ A/cm}^2$. Dynamic Mechanical Analysis (DMA) indicated that the curing reaction started at about $200 \text{ }^\circ\text{C}$ and proceeded very fast up to $250 \text{ }^\circ\text{C}$. The structural change in the MSSQ films during curing was monitored by following the Fourier Transform Infrared (FTIR) absorption intensity of the Si-O stretching vibration, which showed that the Si-O structure became more asymmetric during curing and/or network formation.

I. INTRODUCTION

Recently, as the feature dimensions of integrated circuits (ICs) continually shrink, the idea of minimizing the RC-delay and the crosstalk between metal interconnects has driven extensive studies to develop materials that possess low dielectric constants [1,2]. Spin-on glass (SOG), called FOX, has been used in IC manufacturing because of their good gap filling capability, good local planarization ability, high thermal stability, and low cost [3-6]. In general, silsesquioxanes have a dielectric constant (k) less than 3.0, which is lower than that of the conventional SiO_2 insulator ($k \sim 4$). Especially, methyl silsesquioxane (MSSQ) has been considered as one of the best candidates for the nanoporous dielectric materials whose dielectric constants are below 2.0 [7].

This paper presents the results for the preparation and electrical properties of cured MSSQ thin films of sub-micron thickness. In addition, we studied the curing conditions and reactions of MSSQ by using Dynamic Mechanical Analysis (DMA) and in-situ Fourier Transform Infrared (FTIR) spectroscopy. The surface morphology and RMS roughness of the cured films was studied using Atomic Force Microscopy (AFM).

II. EXPERIMENTAL

The spin-on films of MSSQ were prepared as follows: MSSQ, purchased from Techneglas Co., Ltd., was dissolved in propylene glycol methyl ether acetate (PGMEA, Aldrich) at various concentrations at room tem-

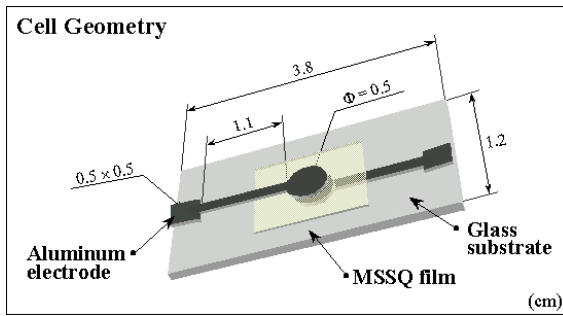


Fig. 1. Cell geometry (Al/cured MSSQ/Al).

perature (RT). It was loaded into a disposable syringe and passed through a $0.2 \mu\text{m}$ PTFE filter (Whatman). The filtered MSSQ/PGMEA solution was spun on glass substrates at 2,500 rpm for 30 sec. On the glass substrate was an Al electrode which had already been deposited by using a thermal evaporator (ULVAC VPC 280). The sample was thermally cured by using the following curing cycle under a N_2 atmosphere: the sample was heated from RT to 50°C for 10 minutes, maintained at 50°C for 10 minutes to evaporate residual solvent, heated from 50°C to 250°C for 2 hours, and then kept at 250°C for 2 hours. Samples with a Metal/Insulator/Metal (MIM) structure were fabricated by evaporating an upper Al electrode, as shown in Fig. 1.

To find the proper curing conditions and to monitor the structural changes in the MSSQ films, we employed DMA (Dupont 983) and FTIR (Midac Prospect), respectively. In the first, we observed a change in the modulus of the MSSQ films during dynamic heating. DMA was run at the resonance mode at a rate of $10^\circ\text{C}/\text{min}$ up to 400°C . We dipped SUS mesh ($1.2 \times 4.2 \text{ cm}^2$) into MSSQ/PGMEA solution and dried it at RT. For the FTIR analysis, we spun the MSSQ/PGMEA solution onto a NaCl crystal and observed in-situ spectra during dynamic heating.

To observe the surface morphology and the roughness

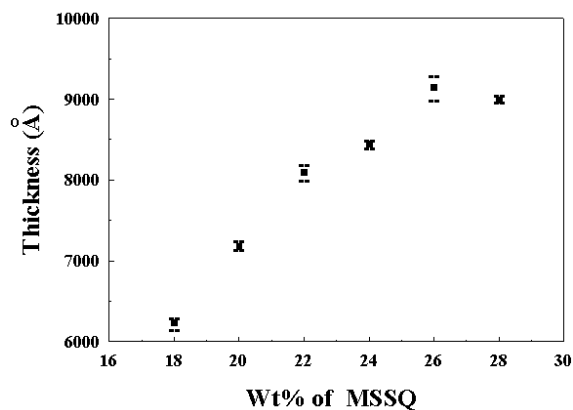


Fig. 2. Thickness change in MSSQ films with concentration.

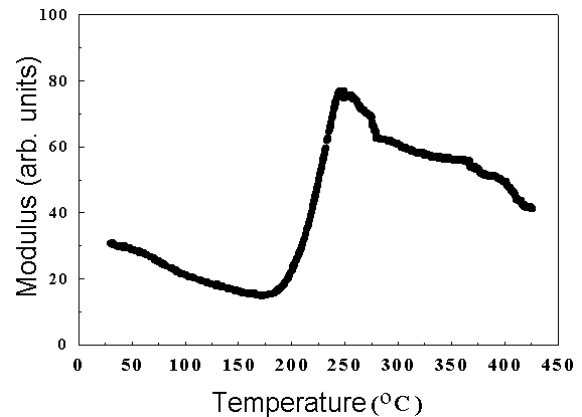


Fig. 3. DMA curve of MSSQ film.

of the cured films, we used AFM. The dielectric constant was measured with an LCR meter (HP model 4194A) interfaced with an IBM PC using LabView software to collect data. The breakdown strength and the leakage current were measured with a source-measure unit (Keithley SMU 236).

III. RESULTS AND DISCUSSION

MSSQ is soluble in common organic solvents such as PGMEA, methyl isobutyl ketone (MIBK), chloroform, chlorobenzene, and toluene. In this research, we used a PGMEA solvent because it has a comparatively high boiling point and is commonly used in the semiconductor industry.

Figure 2 shows the thickness change in the MSSQ thin films spun at various concentrations of MSSQ/PGMEA. The thickness of the MSSQ thin films linearly increased from $6,200 \text{ \AA}$ to $9,000 \text{ \AA}$ over the concentration range from 18 wt% to 26 wt%. After 26 wt%, the thickness of the MSSQ films did not rely on the concentration of the MSSQ/PGMEA solution. In order to study of sub-micron thin-film properties, we prepared films with 18 wt% MSSQ/PGMEA solution which resulted in film thicknesses of $\sim 6,500 \text{ \AA}$.

Figure 3 shows the modulus behavior of MSSQ thin films coated with a SUS mesh. The film became flexible with increasing temperature from RT to 200°C , which was related to a decrease in the modulus. Then, the modulus rapidly increased with increasing temperature up to 250°C , indicative of initiation of a rapid curing reaction. The reason for the sudden fall-off after 250°C is not clear at this point, but it may be due to cracking of the cured film.

The curing reaction was studied by using in-situ FTIR absorption spectra. The MSSQ film was heated from RT to 450°C . The frequency window was in the range of 580 to 1450 cm^{-1} . The two peaks, one at 1140 cm^{-1} and the other at 1080 cm^{-1} , are assigned to the symmetric

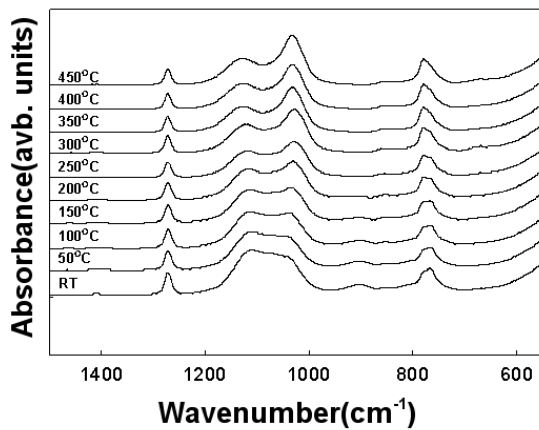


Fig. 4. FTIR spectra of MSSQ film at various temperatures.

and the asymmetric peaks of the Si-O stretching vibration, respectively. Fig. 4 clearly shows the change in the Si-O peaks with temperature. At lower temperature, the intensity of the Si-O symmetric peak (1140 cm^{-1}) was higher than that of the Si-O asymmetric peak (1080 cm^{-1}). However, as the temperature increased, the intensity of the Si-O asymmetric peak became higher than that of the Si-O symmetric peak. It is well known that MSSQ oligomers become MSSQ polymers due to the following reaction during a thermal curing process:

The FTIR result also indicates that the symmetry of the Si-O structure for the oligomeric state was partially broken and became randomized during network formation.

Figure 5 shows the surface morphologies and roughnesses of the deposited Al electrodes and MSSQ thin films. The RMS roughnesses of the Al electrode and the MSSQ thin film were about $5 \sim 40\text{ \AA}$ and $10 \sim 35\text{ \AA}$, respectively. Both of them were comparatively smooth and had good planar surfaces to contact each other.

Figure 6 shows the dielectric constant of the cured MSSQ thin film as a function of the temperature. The

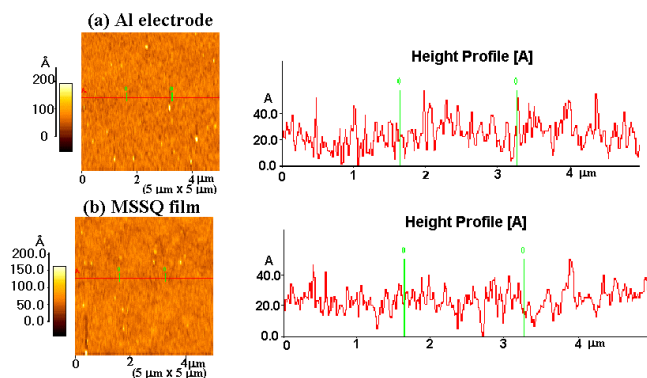


Fig. 5. AFM image and RMS roughness ($5 \times 5\text{ }\mu\text{m}$): (a) deposited Al surface and (b) cured MSSQ film surface.

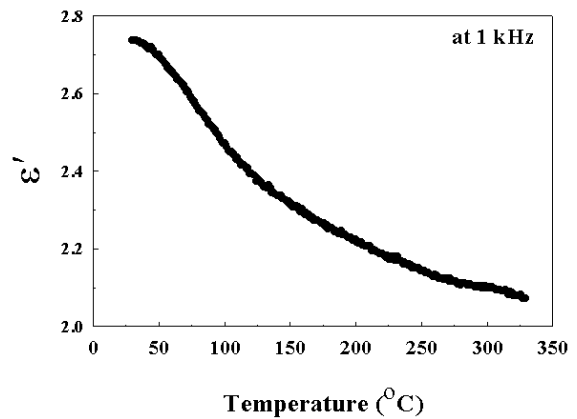


Fig. 6. Dielectric constant of the MSSQ film.

dielectric constant was ~ 2.7 at RT and decreased with increasing temperature. The latter resulted from the fact that the orientations of the dipoles in MSSQ relaxed easily to a random state when the film softened with temperature.

Dielectric materials also need high breakdown strength and small leakage current as an insulator [8]. Fig. 7 shows the I-V curve of a MSSQ thin film to determine its breakdown strength. The current dramatically increased at about 202 V, suggesting that breakdown had occurred. Thus, we found that the breakdown strength was about 2.3 MV/cm .

Figure 8 shows the leakage current of MSSQ thin films. The voltage applied to the cell was 5 V, and the leakage current was taken after a certain period of time, ca. 1,000 sec. About $5.4 \times 10^{-10}\text{ A/cm}^2$ was obtained, which was low enough for use in dielectric materials.

IV. CONCLUSIONS

Polymeric or cured MSSQ thin films were successfully prepared by spinning an oligomeric MSSQ solution

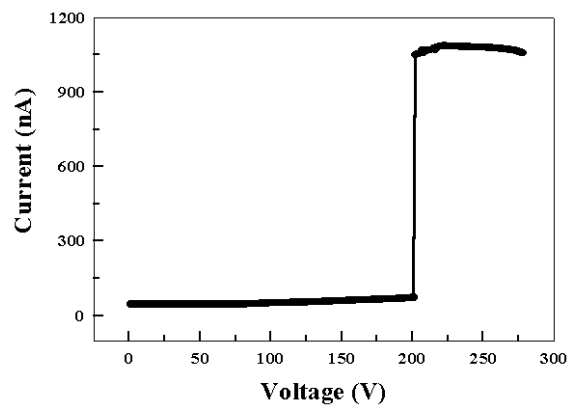


Fig. 7. Breakdown strength of MSSQ films.

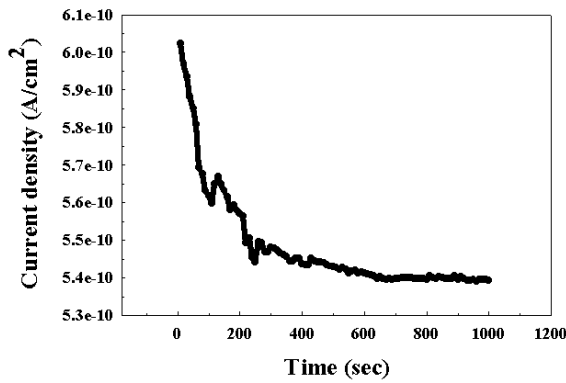


Fig. 8. Leakage current of MSSQ film.

and by thermal curing. DMA results indicated that the curing reaction started at about 200 °C and proceeded quickly up to 250 °C. In-situ FTIR was employed to monitor the change in the structure of the MSSQ during curing and implied that an asymmetry of the Si-O structure developed during curing. The electrical properties of the MSSQ thin films were measured using a MIM-type cell: the dielectric constant was ~ 2.7 , the breakdown strength was above 2.0 MV/cm², and the leakage current was ca. 5.4×10^{-10} A/cm². The present results suggest that MSSQ is a good candidate for a base matrix material that can be used for nanoporous dielectric materials for next generation semiconductor interlayer dielectric (ILD) materials.

ACKNOWLEDGMENTS

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REFERENCES

- [1] The National Technology Roadmap for Semiconductors, Semiconductor Industry Association, San Jose, CA (1997).
- [2] R. R. Tummala, R. W. Keyes, W. D. Grobman and S. Kapur, *Microelectronics Packaging Handbook* (Eds. Rao R. Tummala and Eugene J. Rymaszewski), Van Nostrand Reinhold, Chapman & Hall, New York, USA, 1997), Chapter 9, p. 673.
- [3] L. J. Chen, S. C. Chang and C. M. Wang, 1997 VMIC Conference, ISMIC-107/97/0125(c) (1997).
- [4] K. Numata, T. R. Shera, S. P. Jeng and T. Tanaka, *Mater. Res. Soc. Symp. Proc.* **381**, 255 (1995).
- [5] N. P. Hacker, G. Davis, L. Figge, T. Krajewski, S. Leferts, J. Nedbal and R. Spear, *Mater. Res. Soc. Symp. Proc.* **476**, 25 (1997); G. Sugnhara, N. Aoi, M. Kubo, K. Arai and K. Sawada, 1997 DUMIC Conference, ISMIC-222D/97/0019 (1997).
- [6] J. F. Remenar, C. J. Hawker, J. L. Hedrick, S. M. Kim, R. D. Miller, C. Nguyen, M. Trollsas and Do Y. Yoon, *Mat. Res. Symp. Proc.* **511**, 69 (1998).
- [7] W. Jo, D. C. Kim, H. M. Lee and K. Y. Kim, *J. Korean Phys. Soc.* **34**, 61 (1999).
- [8] Bok-Hee Lee, *J. Korean Phys. Soc.* **34**, 248 (1999).