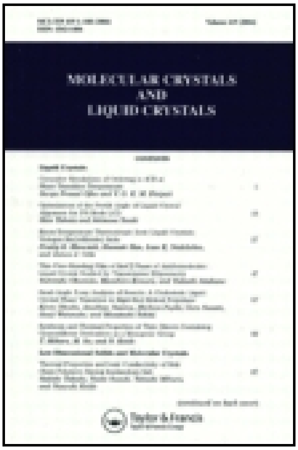

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Dielectric Planarization with Spin-On Glass Films: Characterization and Application

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To cite this article: Jung Ok Park , Jae Gue Lee , Young Jun Hong & Jong-Kee Yeo (1993): Dielectric Planarization with Spin-On Glass Films: Characterization and Application, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 227:1, 339-349

To link to this article: http://dx.doi.org/10.1080/10587259308030987

Mol. Cryst. Liq. Cryst. 1993, Vol. 227, pp. 339–349
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Printed in the United States of America

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Abstract Spin-on glass (SOG) materials were prepared from the acid catalyzed hydrolysis-condensation reaction of tetraethylorthosilicate and methyltriethoxysilane in organic solvents. Siloxane products of different molecular weight, molecular weight distribution, and molecular structure were obtained by adjusting reaction conditions. Various factors such as water content, pH, and reaction time were found to play an important role in controlling the molecular parameters of the reaction products. Properties of these materials were characterized for the spin coated SOG films on both bare and patterned wafers. Effect of the baking temperature and/or molecular parameters were studied in terms of the refractive index, thickness, film shrinkage, stress, crack generation, etc. Control of the molecular weight and hence its distribution and the chemical structure was found to be very important in the preparation of the SOG materials as a good planarization layer.

INTRODUCTION

The fabrication of reliable ULSI circuit structures requires multiple layers of metallization with uniform thickness and subsequent patterning of metal layers with good line width control. The best way to achieve these processing goals is the interlevel planarization of the substrates with dielectric materials prior to the metallization step. Among various techniques for planarization[1-6], techniques based on SOG films are advantageous because of the process simplicity, good adhesion characteristics of SOG, low level of stress and shrinkage in the SOG film, etc.

When the SOG film is dried and baked, however, good adhesion between the SOG and substrate prevents shrinkage in the directon parallel to the film and hence causes shrinkage only in the direction transverse to the film thickness. This results in the buildup of tensile stress in the film and hence SOG films tend to have a low threshold of thickness for cracking.

SOG materials are in general Si-O network polymers in organic solvents, and prepared through the hydrolysis-condensation reaction that employed in sol-gel technology[7,8]. The reaction conditions in SOG synthesis are usually chosen such that the sol polymers are stable toward molecular weight increase over several months. The properties of SOG films can be modified by several techniques, one of which is to incorporate a substituted alkoxysilane, $RSi(OEt)_3$, during the hydrolysis reaction. A high organic content in siloxane SOG offers thick, crack-free films with low dielectric constant, while it reduces thermo-oxidative stability and adhesion property of the films.

SOG solutions used in this study were prepared from tetraethylorthosilicate (TEOS) and methyl triethoxysilane (MTES) in organic solvents. The solutions were spin coated on silicon bare wafers and then the film properties were characterized. The effect of planarization was examined by scanning electron microscope (SEM). The dependence of the material property on the reaction conditions was reported.

EXPERIMENTAL

Preparation of SOG Materials

SOG solutions were prepared to obtain siloxane polymers of different molecular weight (MW), molecular weight distribution (MWD), and molecular structure. It was done by controlling reaction conditions such as molar ratio of H_2O to TEOS and MTES, pH, solvent composition, reactant feeding rate, reaction time, etc. Mole ratio of MTES to TEOS was fixed at 2 to 3. Organic solvent was chosen such that the hydrolysis reaction was not too fast. Condensation reaction was proceeded mainly at 60°C. The final solid contents were adjusted to be about 8 wt% in IPA/acetone/n-butanol mixed solvents in order to keep the coating thickness with desired range.

The molecular weights of siloxane polymers in SOG solutions were characterized by the size exclusion chromatography (SEC) at a flow rate of 1 ml/min using tetrahydrofuran as an eluent at room temperature. The chemical structure of various species at the initial state of the reaction was identified by gas chromatography equipped with mass spectroscopy (GC-Mass).

Portions of SOG materials were dried at 110°C for 2 hours in a drying oven and then thermal property of the resulting powder was studied by Perkin-Elmer DSC-7 at a heating rate of 10°C/min in nitrogen atmosphere.

Characterization of SOG Films

SOG solutions were spin coated on 6 inch silicon bare wafers mainly at 3000 rpm for 20 seconds. Baking of the coated SOG films was carried out under nitrogen atmosphere in two different ways: one, on hot plate for 6 minutes at temperatures up to 300°C, and two, in a horizontal furnace for 30 minutes at temperatures above 300°C. The maximum temperature of baking was limited to 450°C because aluminum was used as interconnection lines. Double layer coating, when necessary, was done by repeating the coating and baking procedures.

The refractive index (RI) of heat treated SOG films was measured by an ellipsometer at a wavelength of 632.8 nm. The film thickness and its uniformity were checked with Nanospec AFT. Film shrinkage was calculated from the difference in the thickness before and after baking.

The change in the chemical structure after baking at each temperature was identified by FTIR with silicon bare wafer as a reference. The residual stress of the baked film was measured using film stress measurement machine after double layer coating.

Application as a Planarization Layer

To patterned wafers made by a 0.7 μm design rule, plasma enhanced chemical vapor deposition (CVD) oxide was deposited in varying thickness of 2000, 4000, and 6000 Å in order to obtain different line spacing. Then SOG solutions were double coated on the CVD layer at 3000 rpm for 20 seconds. Baking of the coated film were proceeded at 80°C for 3 minutes, 230°C for 6 minutes, and 450°C for 30 minutes.

The property as a planarizing layer was examined by looking at the cross sections of the coated wafer with SEM. The leaning angles, % planarization, and crack generation were compared for each double coated SOG films.

RESULTS AND DISCUSSION

SOG Materials

The monomer hydrolysis rate at the initial state of the synthesis was checked for the system consisted of MTES:TEOS:H_2O:H^+ = 1:1:1:0.005 (mole ratio) in IPA. The structure of various species was identified by GC-Mass and then the change in the concentration of the monomers and dimers was plotted as a function of reaction time in Fig. 1. Here, M and T were used to represent the total concentration of monomeric

MTES and TEOS, respectively, including all the hydrolyzed, transesterified, and unreacted species. Also MM, MT, and TT were for dimers of corresponding composition, while D and B in the paranthesis represented the dropping and batch addition of MTES monomer to the solution of TEOS. It was shown that MTES was hydrolyzed faster than TEOS as expected, and monomer consumption was higher when MTES was added dropwise. It was also shown that codimer (MT) was produced in larger quantity by dropwise addition of MTES than batch addition. From these results, it was expected that the technique of dropwise addition of MTES would produce siloxanes with higher MW and MWD than the batchwise addition.

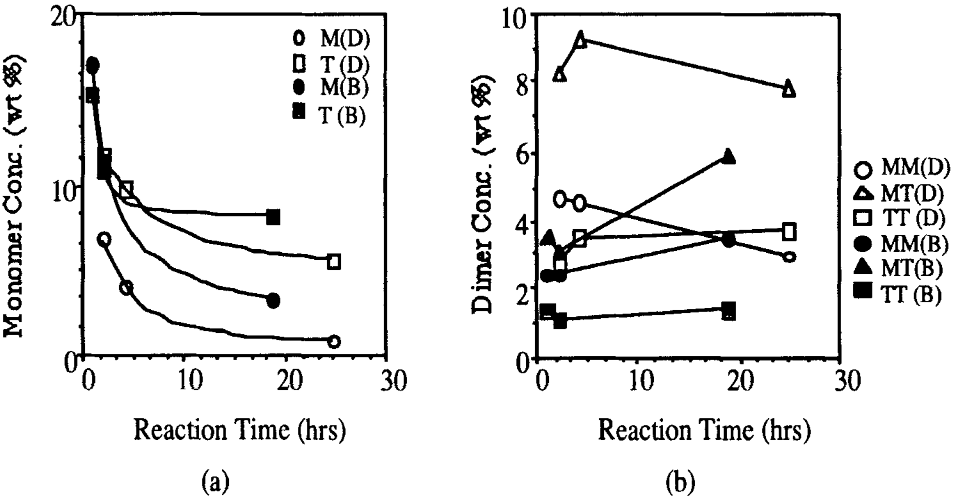


FIGURE 1 Change of reaction species as a function of time at the early stage of SOG synthesis: (a) monomer and (b) dimer concentration.

The MW and MWD of siloxane products in SOG-1 ~ 4 were shown in Fig. 2 and Table I. In the preparation of the first three SOGs, ie. SOG-1 ~ 3, the monomers and some solvent were placed in the reaction vessel and then the mixture of water, acid and more solvent was slowly added. Reaction was enhanced by heating the mixture to 60°C. Different materials were obtained by varying the amounts of water and acid. Among these three, SOG-1 showed the smallest MW and MWD.

The SOG-4 was prepared using the same reactant composition as for SOG-3, but MTES as well as the mixture of water, acid, and solvent was added dropwise into TEOS solution. In this case, the feeding rate of the acid was also much slower than the

SOG-3. The MW and MWD of SOG-4 were shown to be larger than SOG-3 as expected from the result mentioned above. The structure of siloxane polymers in SOG-4 was expected to be more branched than that in SOG-3 but was not confirmed.

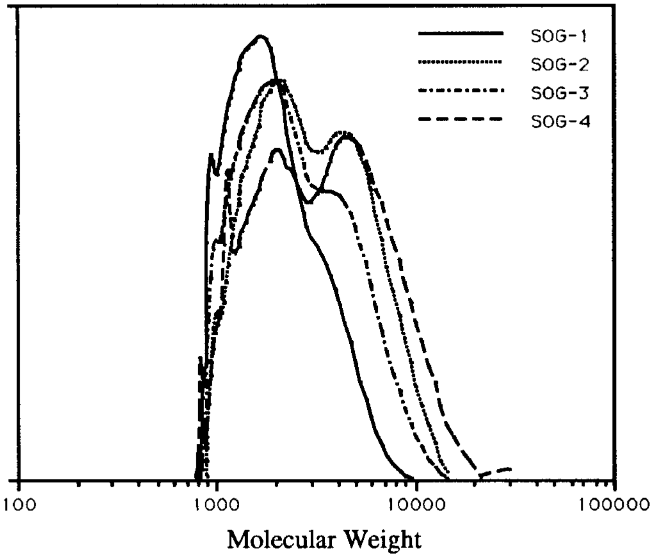


FIGURE 2 Size exclusion chromatographic results for various SOG solutions.

TABLE I Molecular weight and its distribution from SEC result.

Materials	M_n	M_w	M_z	M_w / M_n
SOG-1	1520	1940	2680	1.28
SOG-2	2080	3130	4870	1.51
SOG-3	1790	2560	3910	1.43
SOG-4	2060	3500	6000	1.70

Differential scanning calorimetry of dried SOG materials was shown in Fig. 3. It was reported[9] that thermal responses up to 400°C were due to the desorption of the physically adsorbed solvents, decomposition of the residual alkoxy groups, and the alcohol condensation between the silanol and residual alkoxy groups. The SOG-4, prepared by dropwise feeding of MTES, showed much bigger and broader peak in this region. It implies the particular condition used for the preparation of SOG-4 was not properly adjusted. In general, the breadth of the endothermic peaks at 250 ~ 400°C was in the order of MWD.

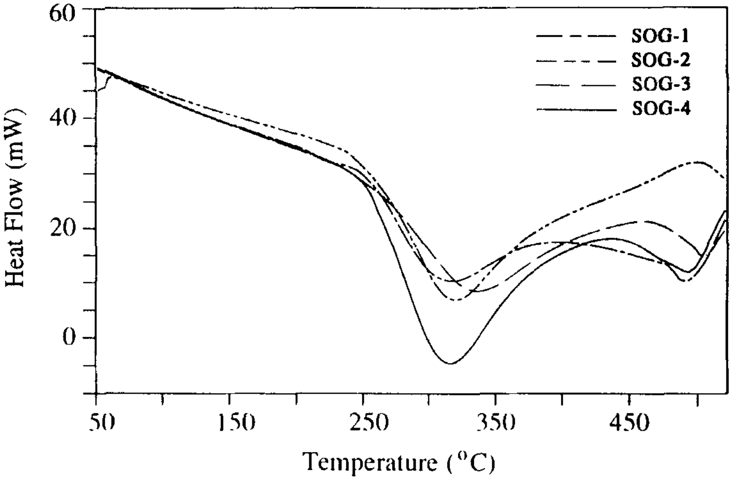


FIGURE 3 Differential scanning calorimetry of SOG materials at a heating rate of 10°C/min under nitrogen atmosphere.

Film Properties

The refractive index and the thickness of the films were plotted as a function of baking temperature in Fig. 4. The values of RI varied in the range of 1.471 ~ 1.484 right after coating, but decreased to 1.375 ~ 1.407 as the baking temperature increased. The SOG material of smallest MW and MWD, SOG-1, exhibited the largest RI throughout the whole range of baking temperature. As the baking was advanced, the thickness of the film also decreased.

In another set of synthesis, samples were taken out at different reaction time to examine the dependence of the film shrinkage on the MW of the homologous species. It was shown in Fig. 5 that the film shrinkage decreased as MW increased during low temperature baking but increased as the baking temperature became higher. The overall shrinkage increased as the MW increased. The MWD also increased as the molecules grew larger.

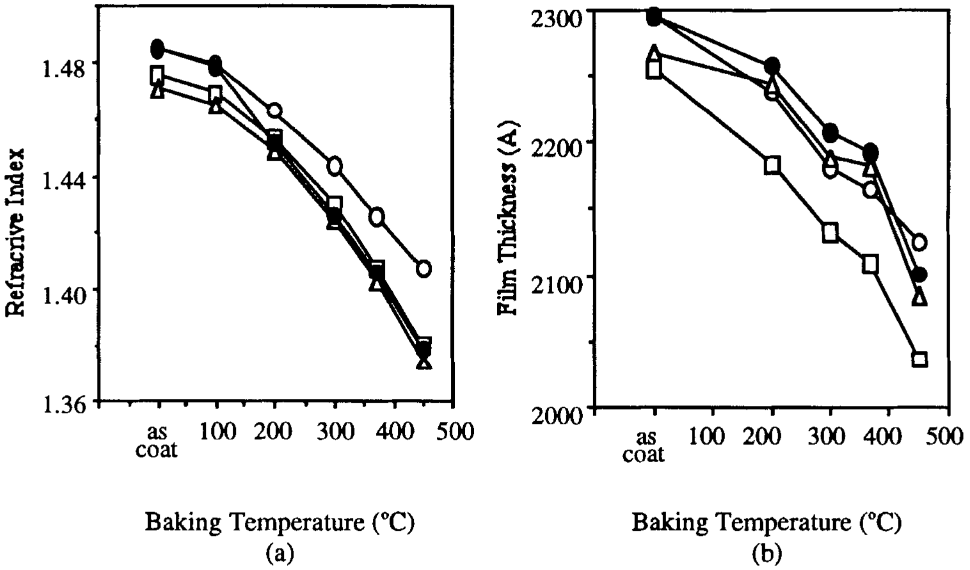


FIGURE 4 Effect of the baking temperature on (a) the refractive index and (b) the thickness of the films. Each symbol denotes SOG-1 (○), SOG-2 (△), SOG-3 (●), and SOG-4 (□).

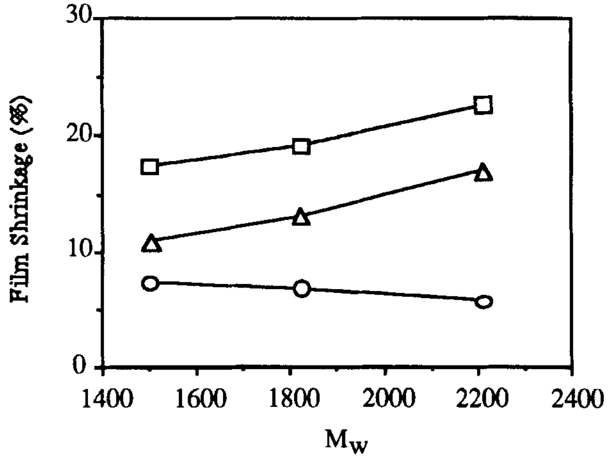


FIGURE 5 Film shrinkage as a function of molecular weight: between as coat and 230°C (○), 230°C ~ 450°C (△), and as coat ~ 450°C (□).

Since the baking temperature was relatively low, one may expect to have significant amounts of residual silanols and absorbed water. This was checked by FTIR as shown in Fig. 6. The broad absoprtion peak at 3100~3600cm^{-1} was due to Si-OH, while the peak at around 930cm^{-1} was for intermolecular hydrogen bonded Si-OH. Absorption by CH_3 appeared as sharp peaks at 1280 and 2980cm^{-1}. The Si-O stretch peak was broad and complex at 1000~1250cm^{-1} due to the variety of the Si-O species produced. Entrapped water was expected to absorb IR at around 1600cm^{-1}.

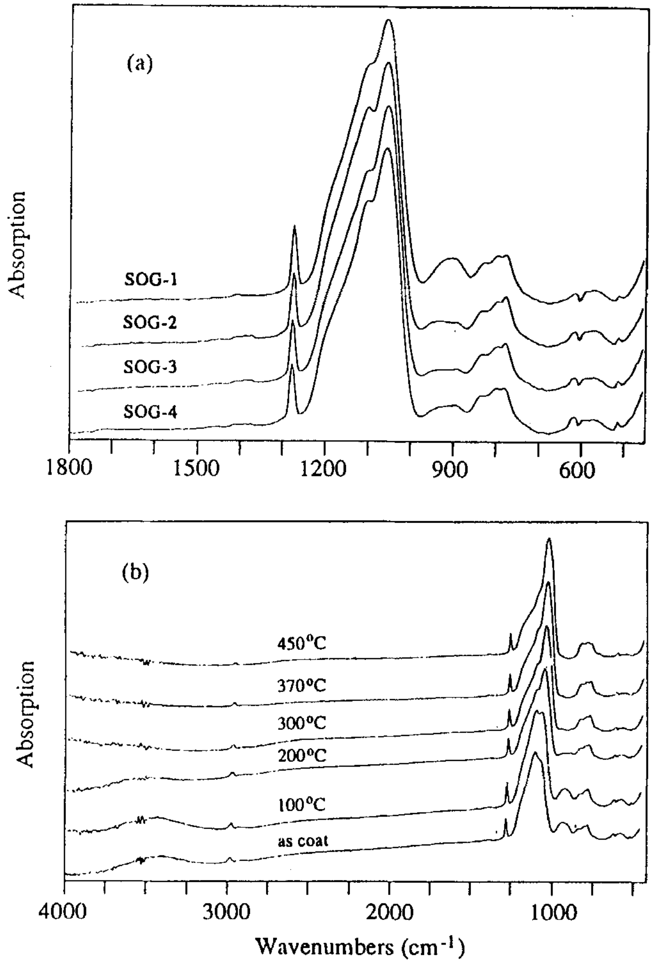


FIGURE 6 FTIR spectra of SOG films: (a) SOG-1 ~ 4 baked at 200°C, and (b) SOG-3 baked at different temperatures.

Relatively speaking, SOG-1 contained largest amount of Si-OH bonds in as coated films and even after 200 °C baking (a). This may be due to the fact that the MW of SOG-1 was the lowest, meaning the condensation was minimum, and hence there remained more unreacted OH groups than the others. As the baking was proceeded at higher temperature, the Si-O peaks became skewed to lower wavenumbers (b). It was also found that there was no detectable amount of silanol or water after the baking at T> 300°C and the CH_3 groups were not destroyed up to 450°C.

The residual tensile stress in the baked double coat SOG films was listed in Table II. The SOG-4 showed the highest level of stress, while the other three SOGs showed about the same level of stress within the experimental error. Since the overall film shrinkage was also the highest for SOG-4 and decreased in the order of SOG-3 ~ SOG-2 > SOG-1, it was expected that SOG-1 would have the best crack resistance and SOG-4 the worst. This was observed to be true as shown below.

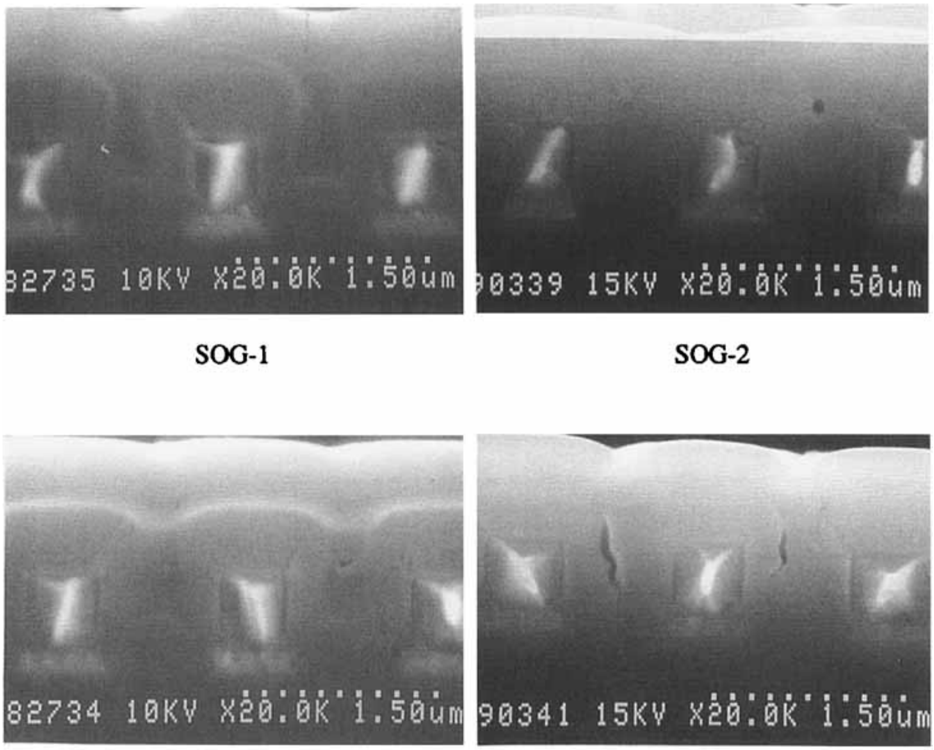
TABLE II Tensile stress of the double coated SOG films after final baking.

Materials	Stress (dyne/cm^2)
SOG-1	1.09×10^9
SOG-2	1.13×10^9
SOG-3	1.07×10^9
SOG-4	1.24×10^9

Planarization Properties

The CVD deposited wafers were found to have the line spacing of 6500 ~ 3500 Å with aspect ratio of 1.31 ~ 2.45. After double coating and baking of SOG materials on these wafers, the cross-sections were examined with SEM as shown in Fig. 7. As a measure of planarization, leaning angles and % planarization were calculated from the cross-sectional photographs and listed in Table III. Good planarization would be manifested by low leaning angle and high % planarization.

It was shown that SOG-1 showed the best performance as a planarization layer, while SOG-2 & 3 caused some voids and SOG-4 had poor crack resistance. This observation was in agreement with the expectation we made from the shrinkage and the stress results discussed above.



SOG-1 SOG-2

SOG-3 SOG-4

FIGURE 7 Scanning electron microscopy for double coated SOG on 6000 Å CVD layer.

TABLE III Properties of SOG materials as a planarization layer.

Materials	Leaning angle (degree)	% Planarization
SOG-1	15.0	88.9
SOG-2	30.5	80.4
SOG-3	25.5	83.3
SOG-4	28.0	82.6

CONCLUSIONS

The hydrolysis-condensation reaction were controlled to achieve SOG materials with different molecular parameters by varying the amount of water and acid, the feeding rate, the reaction time, etc. The nature of the silicone polymer products was shown to be largely dependent on the reaction conditions.

As the reaction continued to give larger molecules, the MWD also became larger. Even at fixed reaction time with the same concentration of MTES and TEOS, MW and MWD could also be varied by changing the amount of acid and water and their feeding rate.

The MW, MWD, and hence the molecular architecture were found to play very important roles in modifying the material properties of SOG. Within the MW range of this study, it was shown that low MW materials offered better SOG performance in terms of the film shrinkage, planarization, crack resistance, etc.

Effects of other factors such as surfactant, reaction temperature profile, and mole ratio of MTES and TEOS are to be studied further. Dielectric properties, etch rate, and plasma resistance are also under study.

Authors wish to thank Dr. D. Y. Yang and Mr. S. R. Song of Goldstar Electronics for their invaluable help throughout J. G. Lee's stay at their site. Without their facilities, encouraging discussion and assistance, this work might have been far less progressed.

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