

ORMOSIL Films: Properties and Microelectronic Applications

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Abstract. The properties, as well as some issues of microelectronic applications of organically modified silicate (ORMOSIL) films, prepared by cohydrolysis in various proportions of tetraethoxysilane (TEOS) and phenyltriethoxysilane (PTEOS), or diphenyldiethylhexyloxydiethoxydisiloxane (DPS)¹, are discussed.

Keywords: organically modified silicates, thin film, refractive index, electrical properties

1. Solution Preparation and Film Formation Process

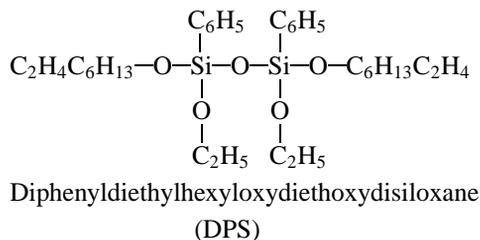
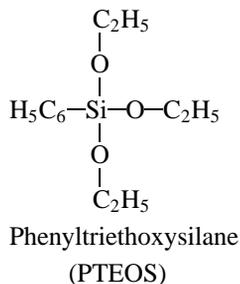
The initial solutions were prepared by dissolving TEOS in *n*-butanol in the presence of some water and HCl. The equivalent SiO content was 6 wt.% and the molar ratio of components was $[H_2O]:[HCl]:[TEOS] = 6:0.04:1$. After prehydrolysis of the initial solution during 5 min, PTEOS or DPS were added. The volume fraction of the added component was 10, 20 or 40% of the TEOS volume in the initial solution (the calculated Ph/Si ratios were 0.085, 0.156 and 0.270, in the case of PTEOS, and 0.069, 0.129 and 0.230, in the case of DPS).

The films were prepared by spinning on silicon wafers with a following bake at 150°C during 3 min (hot plate) and a final anneal at $T_a = 200, 450$ or 600°C, during 20 min. Multiple application with the intermediate

bake was used for thicker film preparation; (two-fold coatings were used for electrical measurements, and three-fold ones for IR spectra). Aluminum electrodes were formed by lithography process, for electrical measurements.

2. IR Spectra

IR spectra of the films were measured with a Perkin-Elmer 1720 spectrometer in the range from 4000 to 400 cm^{-1} . IR spectra of the silicate films are typical of silicate materials prepared by sol-gel techniques and show the presence of hydroxyl groups. Modification of silicate with organic leads to the production of typical phenyl infrared bands, the magnitudes of which increase with increasing organic content (see Fig. 1). The IR spectra of the films prepared from PTEOS and



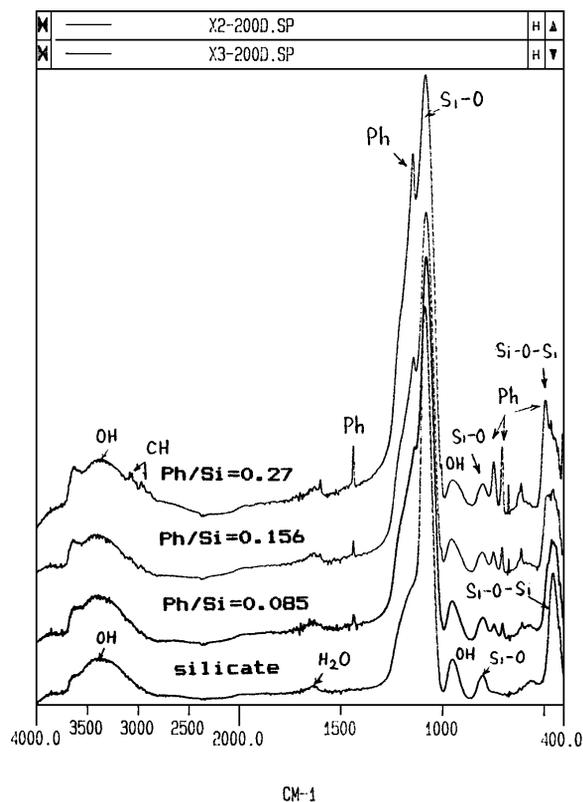


Figure 1. IR spectra of ORMOSILS films with the different phenyl content (heat treatment temperature 200°C).

DPS have therewith practically no difference, indicating full removal of ethylhexyl groups during hydrolysis and polycondensation of DPS.

The heat treatment of the films at 450°C does not cause the spectra to change compared to the spectra of the films treated at 200°C, but annealing at 600°C leads to the destruction of phenyl radicals, accompanied by some densification of the silicon-oxide skeleton. This spectrum is similar to the silicate one, but it still contains some organic residues, as a result of phenyl thermodestruction.

3. Ellipsometry Study

A modification of silicate matrix by phenyl groups leads to increasing film thickness and refractive index, and to decreasing film shrinkage during heat treatment (see Fig. 2). The increase of film thickness is mainly caused by increasing film-forming component concentration. It is very interesting that the refractive index shows a nonlinear increase with increasing phenyl

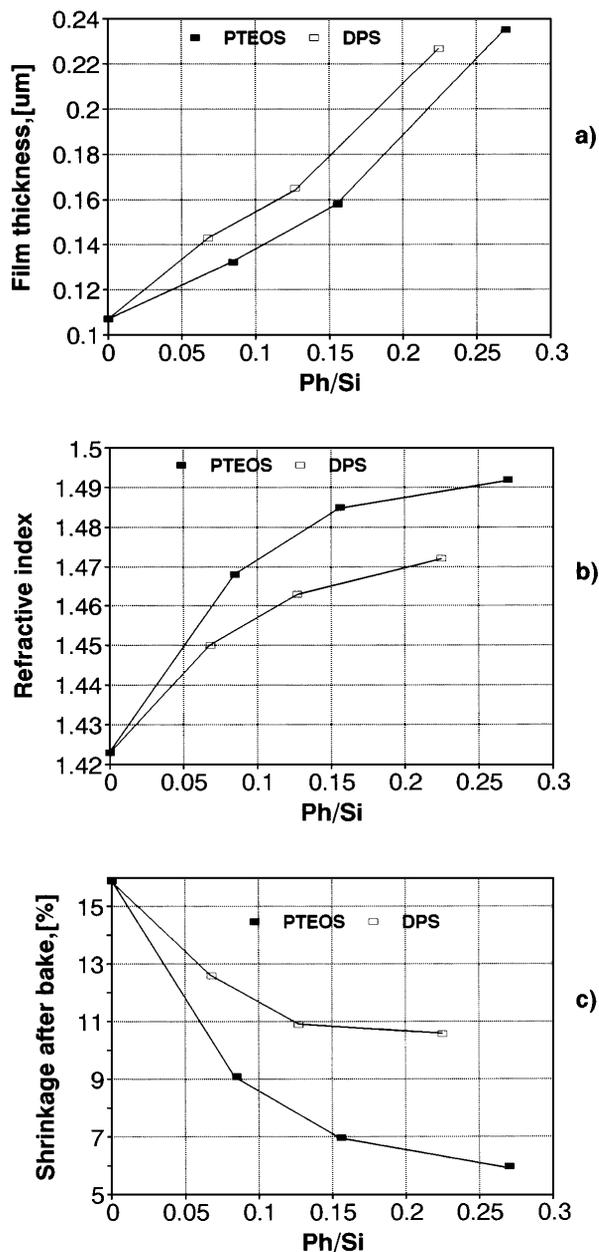


Figure 2. The thickness (a), the refractive index (b), and the shrinkage (between 200 and 450°C heat treatment) of ORMOSILS films as a function of Ph/Si ratio.

content, in contrast to, for example, methylmodified silicates whose refractive index linearly decreases with the methyl content [1]. The increase in the refractive index of phenylmodified silicate films is due to the high refractive index of phenyl radicals (e.g., the refractive indices of PTEOS and methyltriethoxysilane are 1.49 and 1.34, respectively [2]). A nonlinear character of the

refractive index increase indicates decreasing volume density when incorporating phenyl radicals into silicate matrix. As it might be shown from the Lorentz-Lorenz relationship for mixtures, in the case of decreasing volume density, the curve of the refractive index of the mixture is convex upwards, similar to the present experimental data (for details see [3]).

The increase of silicon-carbon bonds leads to a blocking of some directions of polycondensation and to reduction of the film shrinkage. The film shrinkage decreases from 16% for silicate film, to 6% for ORMOSIL film. It should be noted that a reduction in the film shrinkage with Ph/Si content occurs, in spite of increasing film thickness, whereas an increase in the film thickness of silicate films leads to significant increase of their shrinkage (see e.g., [4]). A rise in annealing temperature upto 600°C leads to a sharp increase of the film shrinkage and to a reduction of their refractive index, due to organic decomposition, consistent with the IR spectroscopy data. It should be stressed that the films prepared from PTEOS-based solutions have lower shrinkage (especially for high Ph/Si contents) than those prepared from DPS. This testifies that the PTEOS molecule is more mobile to block polycondensation chains than the DPS molecule in which two phenyl groups are rigidly fixed in the neighborhood.

4. Electrical Properties

The dependence of the dielectric constant and the loss tangent, measured at 1 MHz, for the films annealed at 450°C, as a function of phenyl to silicon ratio, are shown in Figs. 3(a) and (b). High hydroxyl and water content in the silicate film cause unusually high dielectric constant and loss tangent. The value of the dielectric constant of silicate film is 11.7 and the loss tangent reaches 0.19. Similar results, indicating the strong influence of hydroxyls on the dielectric properties of sol-gel silicate films, were reported earlier (e.g., [4]). Modification of silicate with phenyl radicals leads to a practically constant dielectric constant and loss tangent up to the values of about 3.5 for dielectric constant and 0.02–0.05 for loss tangent, with decreasing Ph/Si ratio. The conceivable reason for this may be the decrease of material density when phenyl groups are incorporated into the silicate matrix, as evidenced, in particular, by the dependence of refractive index upon the phenyl content, as well as the decrease of hydroxyl content, as demonstrated by the IR spectra. The semiconductor-dielectric interface was studied by capacitance-voltage

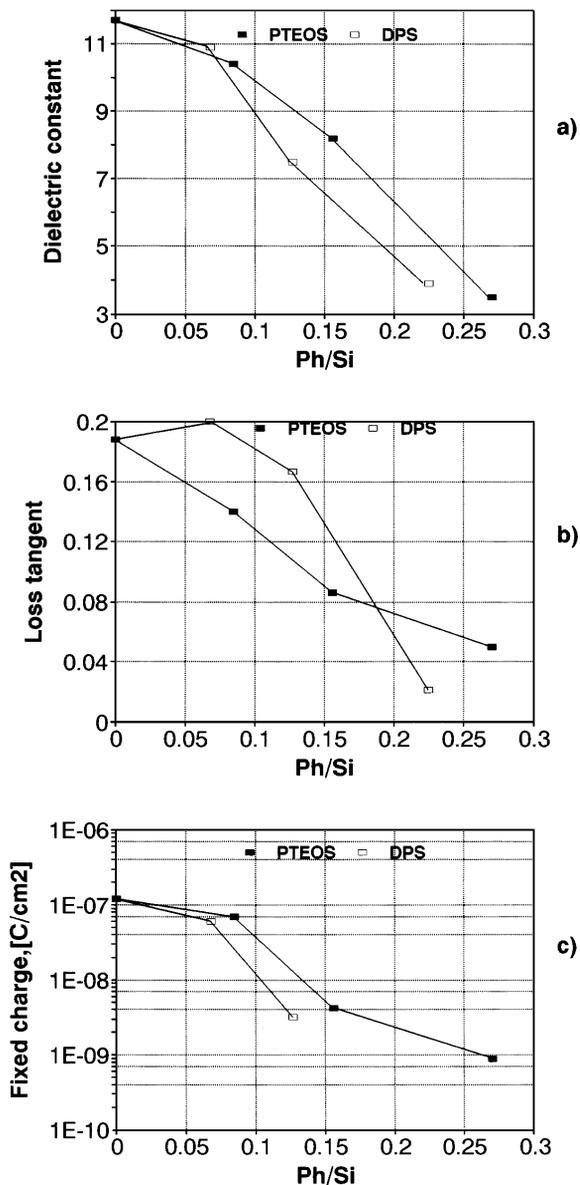


Figure 3. The dielectric constant (a), the loss tangent (b), and the fixed charge (c), of ORMOSILS films as a function of Ph/Si ratio.

(CV) measurements at the frequency of 1 MHz. Polarizability of hydroxyls causes a counter-clockwise hysteresis (injection type) of CV characteristics of silicate films and a high value of the fixed charge (Fig. 3(c)). As the phenyl content in the increases, this hysteresis first goes down, but then changes its direction (polarization-type hysteresis). Most likely, the reversal of hysteresis direction is associated with the polarization of phenyl radicals in high electric field, which is opposite to

hydroxyls. The value of the fixed charge is reduced, with increasing organic content, from $1.3 \cdot 10^{-7}$ C/cm² for silicate film, up to 10^{-9} C/cm², for phenylmodified silicate film.

5. Application of Phenylmodified Films in the Process of Planarization of Multilevel Interconnections

One of the possible applications of ORMOSIL films is the process of planarization of multilevel interconnections of integrated circuits (ICs). Decreasing of IC element sizes complicates the topography relief, with the result that subsequent metal layer is broken or thinned, leading to decreasing yield and reliability of ICs. Thus, planarization or smoothing of topography relief is a crucial point in the fabrication technology of state-of-the-art ICs.

Silicate films have a low cracking resistance over surface topography, due to high shrinkage during bake. Because of this, only thin films (usually 0.1–0.2 μm) on not too high metal relief can be prepared without cracking. To improve the planarization coefficient, two or three-fold applications of silicate films are needed. This complicates the production process and may account for defect generation.

By contrast, phenylmodified silicate smoothing layer gave good planarization coefficient on rather complex topographies: better than two fold application of silicate layers. The films were crack-free over all tested surface topographies. These results suggest that phenylmodified silicates are promising materials in the process of planarization of multilevel interconnections.

6. Conclusions

1. The silicate film prepared by sol-gel techniques represents a porous body with a rigid metal-oxide

skeleton and high hydroxyl content. A high shrinkage and rigid network structure cause their low cracking resistance and poor planarization properties on complex topographies. Electrical and optical properties of silicates are mainly determined by hydroxyl groups.

2. Phenyl radicals, introduced into the silicate network, reduce cross-linking in the polymer structure, their density and hydroxyl content. These provide low shrinkage, high cracking resistance, low dielectric constant and loss tangent of ORMOSIL films. Phenyl radicals have good thermal stability, but, at high concentration, they may develop mobile charges due to their polarizability. The PTEOS molecule is more effective to block polycondensation chains than the DPS one, in which two phenyl groups are rigidly fixed in the neighbourhood. The results obtained suggest that phenylmodified silicates are promising materials for the planarization of multilevel interconnections.

Acknowledgments

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