

Structure, properties and applications of phenyl-modified silicate films

Konstantin A. Vorotilov^a, Vladimir A. Vasiljev^a, Michael V. Sobolevsky^a,
Natalia I. Afanasyeva^b

^a *Moscow Institute of Radioengineering, Electronics and Automation, 117454, Vernadsky prosp., 78, Moscow, Russia*

^b *Institute of Spectroscopy RAS, 142092, Troitzk, Moscow Region, Russia*

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Abstract

Organically modified silicate films prepared by sol-gel techniques have been studied. The silicate structure has been modified by phenyl radicals. The films were prepared by cohydrolysis in various proportions of tetraethyloxysilane and phenyl triethoxysilane or diphenyl diethylhexyloxy diethoxydisiloxane. It is shown that phenyl radicals introduced into the silicate network reduce cross-linking in polymer structure, their density and hydroxyl contents. These provide low shrinkage, high cracking resistance, and low dielectric constant and loss tangent of phenyl-modified silicate films. Some questions of applications of such films in the process of planarization of multilevel interconnections are briefly discussed as well.

Keywords: Electrical properties and measurements; Metallization; Optical properties; Planarization; Structural properties

1. Introduction

Organically modified silicate films (ORMOSILS) are the new type of inorganic-organic hybrids proposed about ten years ago by Schmidt and intensively developed during the last few years in sol-gel science and technology. These materials represent a structure in which organic fragments are built in the inorganic metal-oxide matrix which determines unique properties of such materials (see, for example, Refs. [1-3]). One of the ways of ORMOSILS synthesis is a cohydrolysis of alkoxides and organically substituted alkoxy silanes (alkoxy siloxanes). One or more silicon to carbon bonds, being resistant to hydrolysis, block some directions of the polycondensation reaction that gives lower shrinkage of ORMOSILS with respect to oxides prepared from alkoxide precursors. It is clear that the type, concentration, and spatial arrangement of organic groups within the metal-oxide skeleton will substantially determine the material properties. Thus, practical applications of the inorganic-organic hybrids need fundamental investigations of their structural and physical peculiarities.

The present work deals with the study of optical and electrical properties of silicate films modified by structure fragments containing a phenyl group, as well as with the application of such films in the process of planarization of

multilevel interconnections of ICs. One of the reasons for the choice of phenyl is its good thermal stability in contrast to, for example, the more detailed examined methyl-modified silicates [3].

2. Solution preparation and film formation process

The film-forming solutions were prepared by cohydrolysis in various proportions of tetraethyloxysilane (TEOS) and phenyl triethoxysilane (PTEOS) or diphenyl diethylhexyloxy diethoxydisiloxane (DPS). The DPS molecule has two phenyl groups bonded with two silicon atoms as well as two hardly hydrolyzable ethylhexyloxy bonds in contrast to the PTEOS one, that may have, as we expected, an effect on the dynamics of the polycondensation process and, as a result, on the structure of the material obtained.

The initial solutions were prepared by dissolving TEOS in n-butanol in the presence of some water and HCl. The equivalent SiO₂ content was 6 wt.% and the molar ratio of components was [H₂O]:[HCl]:[TEOS] = 6:0.04:1. After prehydrolysis of the initial solution during 5 min, PTEOS or DPS was added. The volume fraction of the added component

was 10, 20, 40% of the TEOS volume in the initial solution in the case of using both PTEOS and DPS.

Silicon wafers (diameter, 100 mm; resistivity, $10 \Omega \text{ cm}$; doped with boron; (100) orientation) were purified before film deposition first by $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ (3:2) solution at 140°C during 10 min, rinsed in deionized water and then treated in $\text{H}_2\text{O}_2:\text{NH}_4\text{OH}:\text{H}_2\text{O}$ (1:1:5) mixture at 65°C for 10 min with further rinsing in water.

The films were prepared by spin-on with a following bake at 150°C for 3 min (hot plate) and a final annealing at the temperatures 200, 450, and 600°C during 20 min. Multiple applications 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). Aluminium electrodes were formed by a lithography process for electrical measurements.

The approximate composition of the films after annealing can be expressed as $\text{Ph}_y\text{SiO}_{2-y/2}$, where the calculated values of y were 0.085, 0.156, 0.27 in the case of PTEOS, and $v = 0.069, 0.129, 0.23$ in the case of DPS (these values correspond to 10, 20, and 40% volume fraction of the added components).

3. IR spectra

IR spectra of the films were measured with a Perkin-Elmer 1720 spectrometer in the range from 4000 to 400 cm^{-1} . Fig. 1 shows IR spectra of the silicate film and ORMOSILS films with increasing phenyl content (annealing temperature of the films was 200°C). The IR spectrum of the silicate film is typical for silicate materials prepared by sol-gel techniques [2]. The known bands at 1080 (with the shoulder at 1200), 800, and 400 cm^{-1} correspond respectively to asymmetric and symmetric Si-O stretching motions, and Si-O-Si bending mode. At the same time the absorption peak at 960 cm^{-1} and the broad band between 3000 and 3800 cm^{-1} , as well as peak at 1635 cm^{-1} show that the film contains a lot of hydroxyl and water molecules.

A modification of the silicate with organics causes infrared bands typical for phenyl, whose magnitudes increase with phenyl content increasing: 475 cm^{-1} (the peak at 460 cm^{-1} is split and with the increase of phenyl content it moves towards lower frequencies), 705, 750, 1140, 1440 (Si-Ph vibrations [4]) as well as a number of shallow peaks at 2960- 3075 cm^{-1} (CH vibrations [5,6]). The spectra of films prepared from PTEOS and DPS have therewith practically no difference that indicates full removal of ethylhexyl groups during hydrolysis and polycondensation of DPS with the formation of Si-O-Si siloxane bonds in the network structure.

Unfortunately it is hard to make a quantitative estimation of water content in the films with different organic contents as they have different thicknesses, but the lowering intensity of the absorption band at 960 cm^{-1} (in reference to the Si-O band) with increasing organic content indicates some

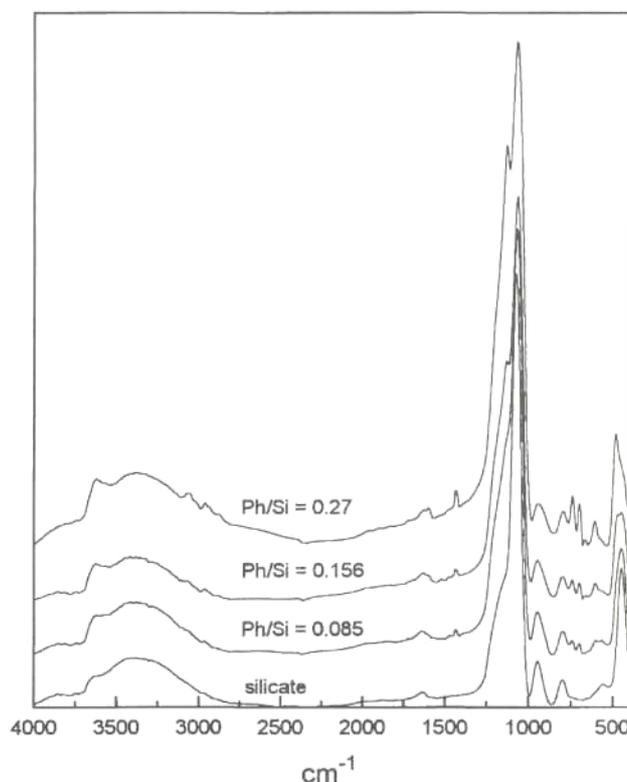


Fig. 1. IR spectra of ORMOSILS films with the different phenyl content (heat treatment temperature 200°C).

decrease of the hydroxyl content in ORMOSILS films (Fig. 1).

A rise in the annealing temperature leads, mainly, to a decrease of the hydroxyl and water absorption bands ($960, 1635, 3000\text{-}3800 \text{ cm}^{-1}$), as well as to a decrease of the shortwave shoulder (1200 cm^{-1}) of the main Si-O band at 1080 cm^{-1} , that suggests structural reconstruction connected with further proceeding of poly condensation reactions during the heat treatment (Fig. 2).

As it can be seen from Fig. 2(b), the heat treatment of the films at 450°C does not cause the spectra to change in reference to the spectra of the films treated at 200°C . An increase of the annealing temperature to 600°C leads to disappearance of the absorption bands of phenyl groups ($475, 705, 750, 1140, 1440, 3075 \text{ cm}^{-1}$) as well as to the shift of the Si-O band from 1075 to $1080\text{-}1085 \text{ cm}^{-1}$, that is indicative of a densification of the silicon-oxide skeleton during destruction of phenyl groups. At the same time, the IR spectra of the ORMOSILS films after annealing at 600°C still differ from the silicate ones: peaks at 2930 and 2960 cm^{-1} remain (asymmetric vibrations of CH_3 groups [4]), and the shortwave shoulder of the Si-O band (1080 cm^{-1}) becomes more pronounced that may be connected also with asymmetric vibrations of CH_3 groups at 1260 cm^{-1} [7]. In addition, a thermodestruction of phenyl groups gives rise to other absorption peaks at 1305 cm^{-1} (conceivably $\text{C}_6\text{H}_5\text{CHO}$ [5]) and 1705 cm^{-1} (conceivably $\text{CH}_3\text{COC}_6\text{H}_5$ [5,6]).

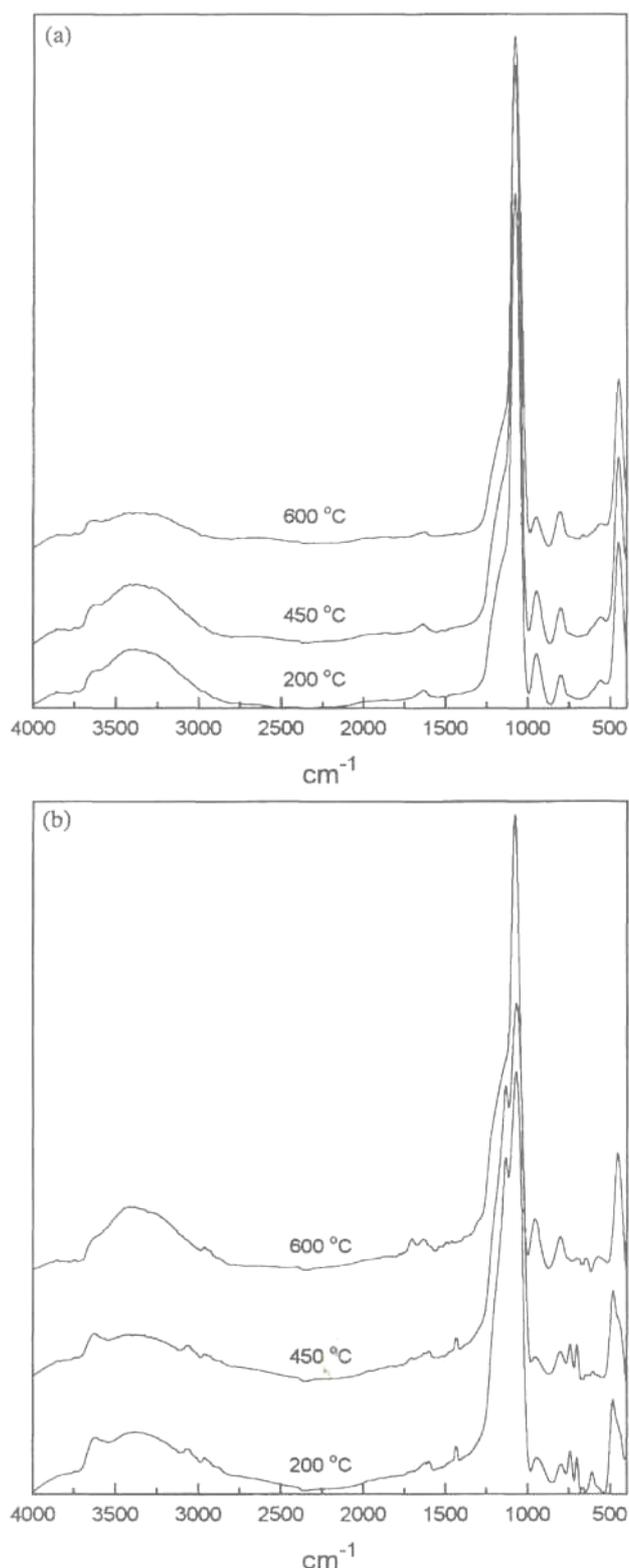


Fig. 2. IR spectra of silicate (a) and ORMOSILS (b) films annealed at different temperatures.

4. Ellipsometry study

The thickness and the refractive index of the films were measured by multiangle ellipsometry at 632.8 nm [8].

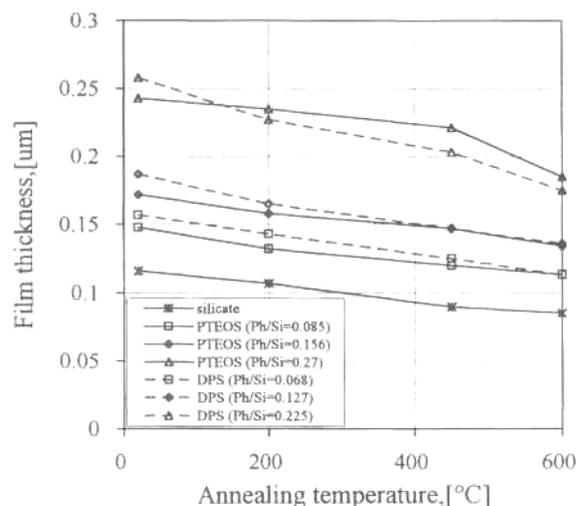


Fig. 3. The dependence of the thickness of ORMOSILS films with different organic contents as a function of heat treatment temperature.

Figs. 3-5 show the dependencies of the thickness, the refractive index and the shrinkage (after deposition and after a bake at 200 °C) of ORMOSILS films with different organic contents upon the heat treatment temperature for the films prepared from PTEOS and DPS. Fig. 6 presents the dependencies of the shrinkage (after bake) and the refractive index on the phenyl to silicon ratio.

Proceeding polycondensation reactions in the films leads to densification of the metal-oxide network with the heat treatment and it is accompanied by significant film shrinkage (Figs. 3 and 5). The most pronounced shrinkage occurs in silicate films (16% shrinkage during heat treatment from 200 to 450 °C—see Fig. 5). At the same time, the refractive index of silicate films only slightly varies with temperature, whereas the calculations on the base of the Lorentz-Lorenz relationship for a porous body show that the 16% shrinkage of silicate film during heat treatment from 200 to 450 °C must give an increase of about 0.08 in the refractive index¹. This suggests that hydroxyls have a greater impact on the refractive index of silicate films than their porosity (see also Ref. [9]).

A modification of the silicate matrix by phenyl groups leads to increasing film thickness and refractive index, and to decreasing film shrinkage during heat treatment process (see Fig. 6). The increase of the film thickness is mainly caused by increasing the film-forming components concentration as well as by volume structural effects. It is interesting that the

¹ According to the Lorentz-Lorenz relationship for a porous body the shrinkage S of material during the annealing process may be expressed as:

$$S = \frac{n_s^2 + 2}{n_s^2 - 1} \left(\frac{n_2^2 - 1}{n_2^2 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right)$$

where n_s , n_1 , n_2 are the refractive indices of the solid skeleton, and material before and after heat treatment, respectively.

In the case of small variations in refractive index the shrinkage of the porous body must cause the change in the refractive index:

$$n_2 - n_1 \approx S \cdot \frac{(n_s^2 - 1)(n_s^2 + 2)}{6n_s}$$

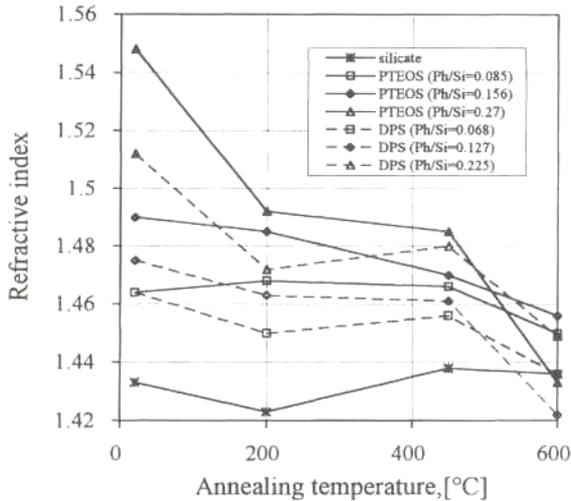


Fig. 4. The dependence of the refractive index of ORMO-SILS films with different organic contents as a function of heat treatment temperature.

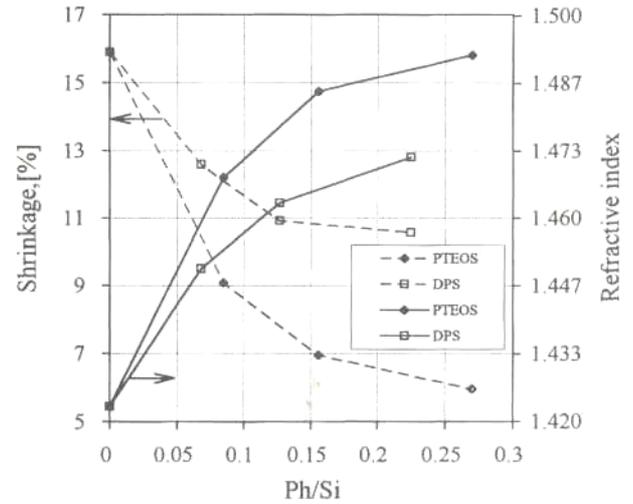


Fig. 6. The shrinkage between 200 and 450 °C heat treatment (dotted line) and the refractive index (solid line) of ORMO-SILS films as a function of Ph/Si ratio.

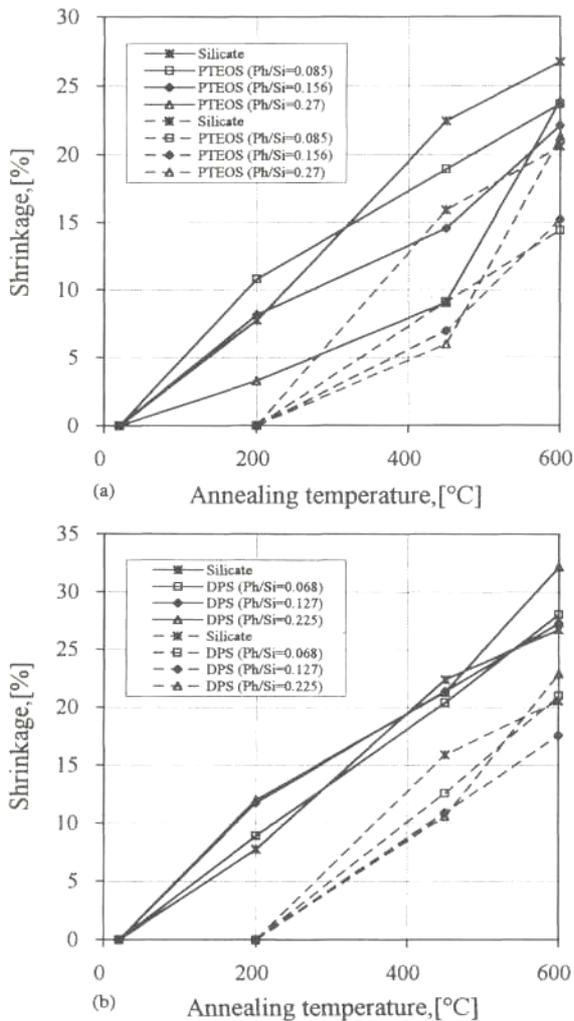


Fig. 5. The dependence of the shrinkage after deposition (solid line) and after a bake at $T = 200$ °C (dotted line) of ORMO-SILS films with different organic contents as a function of heat treatment temperature. For the films prepared with the use of PTEOS (a) and DPS (b).

refractive index shows a non-linear increase with increasing phenyl content, in contrast to, for example, methyl-modified silicates whose refractive index is linearly decreased with methyl content [10]. The increase in the refractive index of phenyl-modified 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 non-linear character of the refractive index increase indicates a volume density decrease when incorporating phenyl radicals into silicate matrix as it might be shown from the considerations of the Lorentz-Lorenz relationship for mixtures. Calculations from the Lorentz-Lorenz relationship show that in the case of a volume density decrease the curve of the refractive index of the mixture is convex similarly to the experimental data².

The increase in the films of silicon to carbon bonds leads to a block of the polycondensation reaction in some directions and to reduce the film shrinkage. The film shrinkage is decreased from 16% for the silicate film to 6% for ORMO-SILS film. It should be noted that a reduction in the film shrinkage with Ph/Si content occurs in spite of increasing the film thickness, whereas an increase of the film thickness of silicate films leads to significantly increasing their shrinkage (see, for example, Ref. [11]). A rise in annealing temperature up to 600 °C leads to a sharp increase of the film shrinkage and to reduction of their refractive index due to organic decomposition that is consistent with the IR spectroscopy data (Section 3).

It should be stressed that the films prepared from PTEOS-based solutions have lower shrinkage (especially for high

² According to the Lorentz-Lorenz relationship the refractive index of material n consisted in the mixture of two materials with the refractive indices n_1 and n_2 , the mass fraction m_1 and m_2 , and the volume density ρ_1 and ρ_2 :

$$n = n_1 + \frac{m_2(n_2 - n_1)}{\rho_2/\rho_1 + m_2(1 - \rho_2/\rho_1)}$$

Ph/Si contents) than those prepared from DPS. This testifies that the PTEOS molecule is more effective to block polycondensation chains than the DPS molecule in which two phenyl groups are rigidly fixed in the neighbourhood.

5. Electrical properties

The dependences of the dielectric constant and the loss tangent measured at the frequency 1 MHz for the films annealed at 450 °C as a function of phenyl to silicon ratio are shown in Fig. 7. High hydroxyl and water content in silicate film causes an anomaly high dielectric constant and loss tangent. The value of the dielectric constant of the 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 [11-13]. Modification of the silicate with phenyl radicals leads to a practically linear decrease in the dielectric constant and the loss tangent with Ph/Si ratio down to values of about 3.5 for dielectric constant and 0.02-0.05 for loss tangent. The conceivable reasons of 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 phenyl content (see Section 4); as well as the decrease of hydroxyl content as demonstrated by IR spectra (see Section 3). Unfortunately, it is hard to estimate the contribution from each components due to the lack of qualitative estimation of the density and the hydroxyl content in phenyl-modified silicate films (we plan to perform such experiments in further work).

The semiconductor-dielectric interface was studied by capacitance-voltage ($C-V$) measurement at the frequency 1 MHz. Polarizability of hydroxyls causes a counter-clockwise hysteresis (injection type) of $C-V$ characteristics of silicate films and high value of the fixed charge (Fig. 8). As the phenyl content in the films is increased this hysteresis first

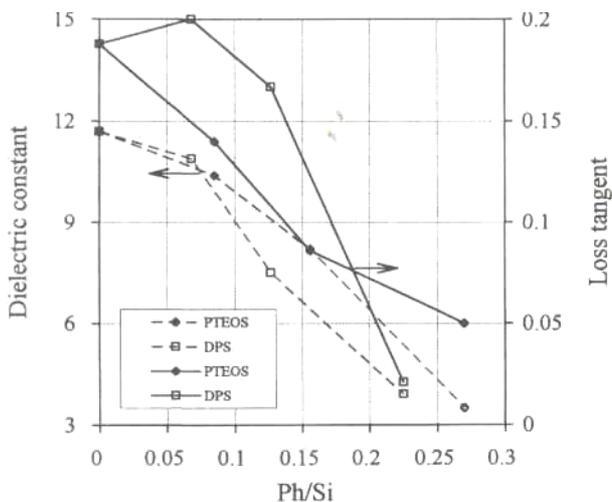


Fig. 7. The dielectric constant (dotted line) and the loss tangent (solid line) of ORMOSILS films as a function of Ph/Si ratio.

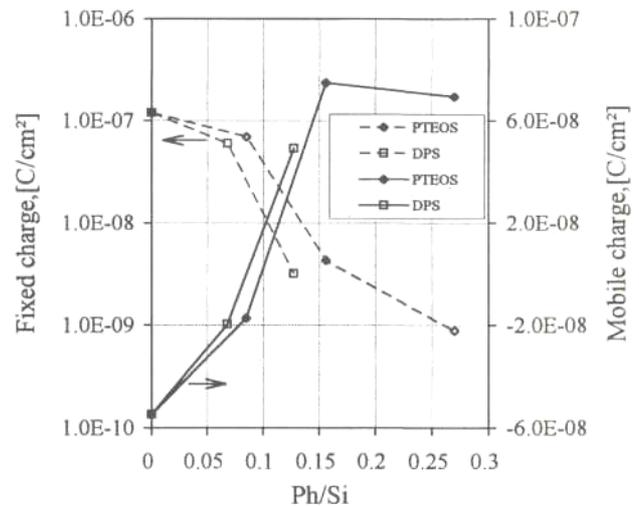


Fig. 8. The fixed charge (dotted line) and the mobile (hysteresis) charge (solid line) in ORMOSILS films as a function of Ph/Si ratio.

goes down, but then changes its direction to the opposite (polarization-type hysteresis). The corresponding hysteresis charge alteration on the silicon-dielectric interface (mobile charge) is shown in Fig. 8, where negative values of mobile charge correspond to injection-type hysteresis, and positive ones to polarization-type hysteresis. Most probably, the reverse of the hysteresis direction is associated with a polarizability 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 $1.2 \times 10^{-7} \text{ C cm}^{-2}$ for the silicate film up to $10^{-9} \text{ C cm}^{-2}$ for the phenyl-modified silicate film. The fixed charge in the films, first in all in silicate films, also causes the distortion of the $C-V$ curve in the high inversion region. In this case, charged centers in the film near the semiconductor-dielectric interface generate inversion of the surface potential of semiconductor that leads to lateral current flow and extending of space charge area [14].

6. Application of phenyl-modified films in the process of planarization of multilevel interconnections

One of the possible applications of ORMOSILS films is the process of planarization of multilevel interconnections of ICs. There are two main versions of the planarization process with the use of spin-on glasses (e.g. Ref. [15]). In a non-etchback process a smoothing silicate or siloxane layer is deposited between two layers of plasma-enhanced CVD oxide; in a partial etchback process a part of the smoothing layer on the top of the lines is etched by a dry etching process to prevent degradation of contacts between metal 1 and metal 2.

Silicate films have a low cracking resistance over the surface topography due to high shrinkage during bake as it may be seen from the micrographs in Fig. 9(a). Because of this only thin films (usually 0.1-0.2 μm) on not too high metal

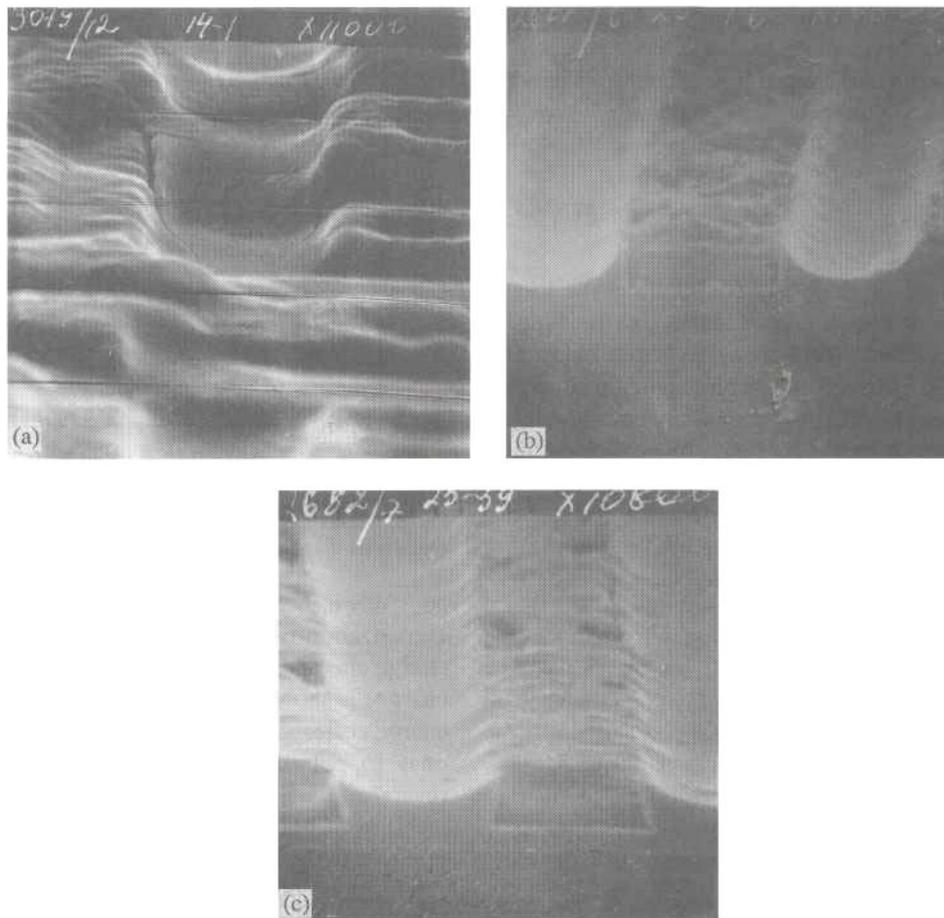


Fig. 9. Silicate films on topography relief (annealing temperature, 420 °C). Cracking (a); one-fold application of silicate film (b); two-fold application of silicate film (c).

relief can be prepared without cracking (Fig. 9(b)). To improve the planarization coefficient a two- or three-fold application of silicate films is needed (Fig. 9(c)). This complicates the production process and may account for defect generation.

The micrograph in Fig. 10 shows a test structure with the phenyl-modified silicate smoothing layer. As can be seen, this layer provides a good planarization coefficient on the rather complex topography: better than a two-fold application

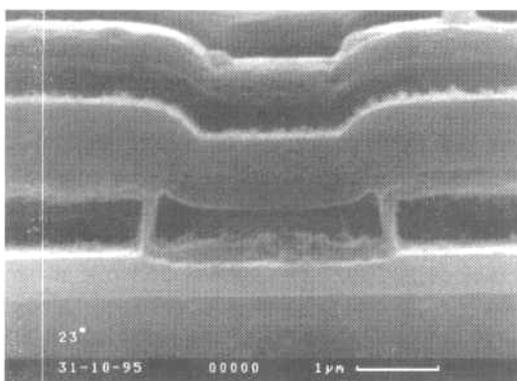


Fig. 10. Micrograph of the test structure with a phenyl-modified smoothing layer.

of silicate layers. The films were crack-free over all the tested surface topographies. All of this suggests that phenyl-modified silicates are promising materials in the process of planarization of multilevel interconnections.

7. Conclusions

1. The silicate film prepared by sol-gel techniques represents a porous body with a rigid metal-oxide skeleton and a high hydroxyl content. A high shrinkage and rigid network structure cause their low cracking resistance and poor planarization properties on complex topography relieves. Electrical and optical properties of silicates are mainly determined by hydroxyl groups.
2. Phenyl radicals introduced into the silicate network reduce cross-linking in a polymer structure, their density and hydroxyl content. These provide low shrinkage, high cracking resistance, and low dielectric constant and loss tangent of ORMOSILS films. Phenyl radicals have good thermal stability, but at high concentration they can develop mobile charge due to their polarizability. The PTEOS molecule is more effective at blocking polycondensation chains than the DPS one in which two phenyl

groups are rigidly fixed in the neighbourhood. The results obtained suggest that phenyl-modified silicates are promising materials for the planarization of multilevel interconnections.

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