

Properties of Sol–Gel Derived Thin Organoalkylenesiloxane Films

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Abstract—We have prepared film-forming solutions for the growth of dense and porous thin organoalkylenesiloxane (OAS) films based on copolymers of methyltrimethoxysilane and 1,2-bis(trimethoxysilyl)ethane (BTMSE) by a sol–gel process. The chemical composition and microstructure of the OAS films have been studied by IR spectroscopy and spectral ellipsometry in relation to the mole fraction of BTMSE and the water : methoxy groups ratio in solution. The results demonstrate that partial substitution of ethylene bridges for silicon–oxygen bonds in OAS leads to distortion of the regular ladder-like structure characteristic of polymethylsilsesquioxane films and the presence of residual silanol groups, which causes an increase in the dielectric permittivity k of the matrix material. The relative porosity in porous OAS films produced via evaporation-induced self-assembly has been shown to be determined by not only the amount of surfactant added but also the presence of a sufficient amount of silanol groups, participating in the attachment of surfactant molecules, in the matrix copolymer solution. In this connection, an important factor determining the structure of the OAS matrix and its pore structure is control over the amount of water involved in the cohydrolysis process. It has been shown that the samples with a relative porosity of 38% prepared from a film-forming solution containing 47 mol % BTMSE ($m = 0.7$) and 30 wt % surfactant have $k \approx 2.3$ and are potentially attractive materials for use as insulators in integrated circuits.

Keywords: thin films, sol–gel method, dielectric permittivity, porosity, organoalkylenesiloxanes, polymethylsilsesquioxanes

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INTRODUCTION

The ability to integrate materials with low dielectric permittivity k (so-called low- k dielectrics) into multi-level metallization systems that ensure interconnection between elements of integrated circuits is a key issue in modern micro- and nanoelectronics because of the necessity to reduce the delay time and heat release [1–3].

Promising materials for applications in 10-nm manufacturing technology metallization systems are organoalkylenesiloxanes (OAS's)—materials in which silicon–oxygen (Si–O–Si) bonds are partially replaced by alkylene (Si–CH₂–CH₂–Si) bonds to improve their electrical [4] and mechanical [5–7] properties.

OAS films can be produced by a sol–gel process, which relies on hydrolysis and polycondensation reactions, typically with the participation of metal alkoxides, and leads to the formation of a metal–oxygen skeleton. Its gradual branching results in sequential structural transformations: solution (sol)–gel–oxide [8].

The formation of a porous structure in such films can be ensured by evaporation-induced self-assembly

using surfactants, which ensure control over the pore structure [9], while maintaining sufficiently good mechanical properties of the films [10].

Unfortunately, the effects of film-forming solution preparation conditions and the Brij 30 surfactant, added to control relative porosity, on the structural perfection and electrical properties of films grown using copolymers of alkylenealkoxysilyls and alkyl-substituted alkoxysilanes have yet to be studied in sufficient detail.

The objectives of this work are

(1) to assess the effect of partial substitution of –CH₂–CH₂– ethylene bridges for silicon–oxygen bonds in dense OAS films based on copolymers of methyltrimethoxysilane (MTMS) and 1,2-bis(trimethoxysilyl)ethane (BTMSE) and prepared under various conditions of cohydrolysis and cocondensation reactions, and

(2) to study the properties of porous OAS films grown via the evaporation-induced self-assembly (EISA) [8, 11] of a surfactant in a wide range of film porosities.

[†] Deceased.

EXPERIMENTAL

As a film-forming solution, we used a solution in which the cohydrolysis and cocondensation of silicon alkoxides (MTMS and BTMSE) in an aprotic solvent in the presence of water and an acid catalyst (HCl) were conducted.

Film-forming solutions for producing dense films were prepared via the acid-catalyzed cohydrolysis and cocondensation of MTMS (98%, Fluka) and BTMSE (96%, Sigma-Aldrich) in tetrahydrofuran (THF) (anhydrous, 99.9%, Sigma-Aldrich) as an aprotic solvent, in the presence of hydrochloric acid (37%, Sigma-Aldrich) and deionized water.

Appropriate amounts of MTMS, BTMSE, THF, water, and the acid were added to a flask fitted with a magnetic stirrer. The mole fraction of BTMSE in the solutions was $v = 25, 33,$ and 47 mol %. The water content per methoxy groups (m) in the solution with $v = 47$ mol % was varied from 0.5 to 0.7. The other solutions had $m = 0.6$. The MTMS : HCl mole ratio was 1 : 0.001. The equivalent Si content of the solutions was 0.5–2 wt %.

To obtain porous films, the Brij 30 surfactant ($C_{12}H_{25}(OCH_2OCH_2)_4OH$, molar mass of 362 g/mol, Sigma-Aldrich) was added to the film-forming solution. The surfactant content was varied in the range $\omega_{\text{surf}} = 30\text{--}60$ wt %. After such a solution is applied to a substrate, the solvent is evaporated. When the surfactant concentration reaches the critical micelle concentration, the surfactant molecules spontaneously self-organize through noncovalent interactions (hydrogen bonding, van der Waals forces, and electrostatic forces) to form liquid-crystal structures, which act as a structure-forming agent for the MTMS–BTMSE copolymer. During heat treatment, the surfactant molecules burn out to form pores in the organosilicon matrix. This ensures a relatively high degree of control over the pore shape, pore size distribution, and structural perfection [11, 12].

Films were produced on KDB-0.005 and KDB-80 boron-doped single-crystal silicon wafers (resistivity of 0.005 and 80 Ω cm, respectively) by spin coating at a spin speed of 2500 rpm. The films were dried in an infrared (IR) flash furnace at a temperature of 200°C for 5 min and then in an isothermal furnace at $t_a = 430^\circ\text{C}$ for 60 min to ensure an essentially complete surfactant burnout. The use of the latter temperature is consistent with process requirements for the integration of OAS films into metallization systems.

The IR spectra of the films produced on the high-resistivity silicon wafers were measured on a Thermo Scientific Nicolet 6700 Fourier transform spectrometer in the range 4000 to 400 cm^{-1} . The thickness d and refractive index n of the films were determined using a SENTECH SE-850 spectral ellipsometer. The angle of incidence of light was 65° . The values of d and n were calculated in the Cauchy model for silicon diox-

ide. The relative porosity ϕ was calculated in the Lorentz–Lorenz model (using $n = 1.46$ for the matrix material). The shrinkage of the films was evaluated from changes in their thickness after heat treatment at 100 and 430°C. In capacitance (C) measurements by a procedure described elsewhere [13], we used an MDC CSM/Win-VF6 measuring system, which included an Agilent 4284A LCR bridge and MDC 802B-150 mercury manipulator with a probe diameter of 790 μm .

RESULTS AND DISCUSSION

The effect of BTMSE content on the properties of the films was studied at a constant water : methoxy groups ratio, $m = 0.6$, using the films with $v = 0, 25, 33,$ and 47 mol % as an example.

Figure 1 shows IR spectra of a dense polymethylsilsesquioxane (PMSSQ) film, whose growth was described previously [14] and those of a dense and a porous ($\omega_{\text{surf}} = 40$ wt %) OAS film. It is known that spectra of porous films may differ significantly from those of dense films as a result of interactions between molecules of some surfactants and the organosilicon matrix, which prevent the formation of a Si–O–Si network structure [15]. Figure 1 demonstrates, however, that the dense and porous films under investigation have identical spectra, except for the shift of the Si–O–Si peak to higher wavenumbers, which is obviously due to the increased porosity [7, 16]. In addition, the spectra of the porous films point to a smaller amount of adsorbed O–H groups, which seem to leave, during heat treatment, the percolated material with an open pore structure that resulted from pore coalescence at $\phi > 0.2\text{--}0.3$ [10]. For this reason, we subsequently analyzed predominantly only the spectra of the dense films, which, however, were normalized not only to the thickness d but also to the density $(1 - \phi)$ of the films [15] in order to take into account the microporosity of the matrix [2]. In Fig. 1, we mark the main absorption bands, which were assigned using previously reported results [1, 2, 5–7, 16]. The spectra presented in Fig. 1 demonstrate broadening of the absorption bands of the OAS films at 1127 and 1033 cm^{-1} , which attests to distortion of the ladder-like structure characteristic of PMSSQ films.

The IR spectra of the dense OAS films grown from solutions differing in BTMSE content are presented in Fig. 2, where the peak corresponds to the Si–O–Si bonds in the network structure and the shoulder at 1127 cm^{-1} arises from the Si–O–Si bonds in a cage-like structure [16]. As would be expected, in the films annealed at $t_a = 430^\circ\text{C}$ the intensity of the absorption bands due to bending and stretching vibrations of the Si–CH₃ bonds at 1275 and 780 cm^{-1} decreases with increasing BTMSE content because of the reduction in the amount of methyl groups in the copolymer.

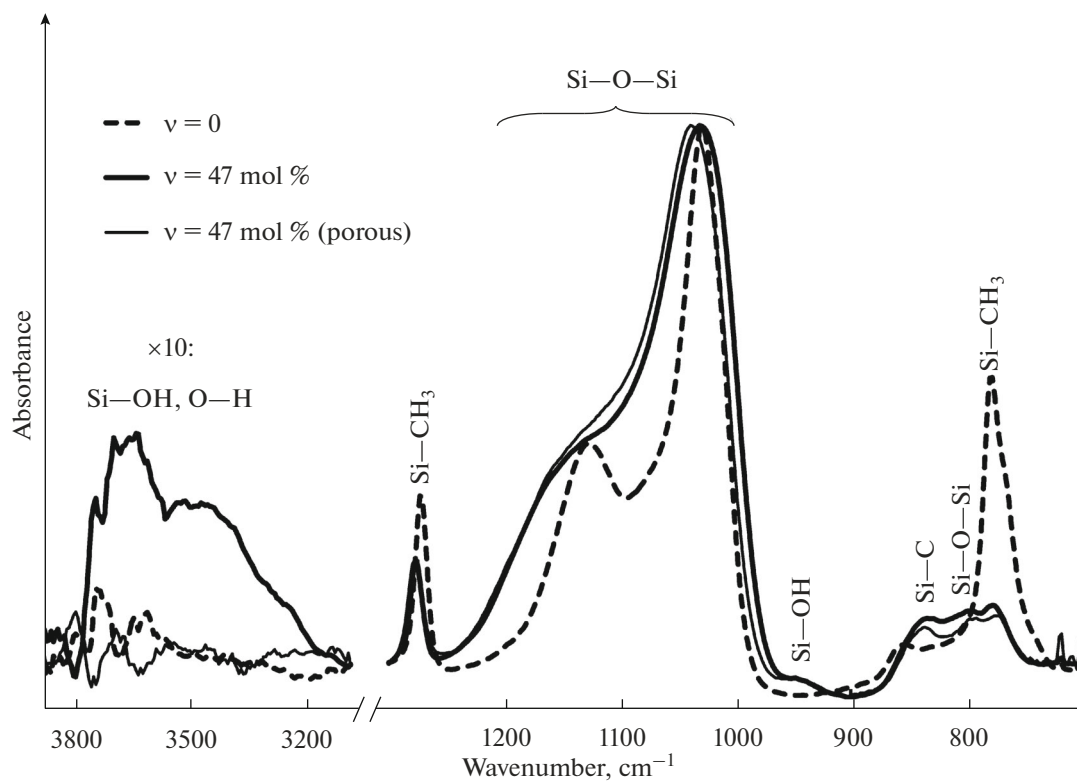


Fig. 1. IR spectra of a dense PMSSQ film ($v = 0$) and a dense and a porous ($\omega_{\text{surf}} = 40$ wt %) OAS film (BTMSE content $v = 47$ mol %, water : methoxy groups ratio $m = 0.7$) annealed at $t_a = 430^\circ\text{C}$. The spectra are normalized to the height of the Si—O—Si band.

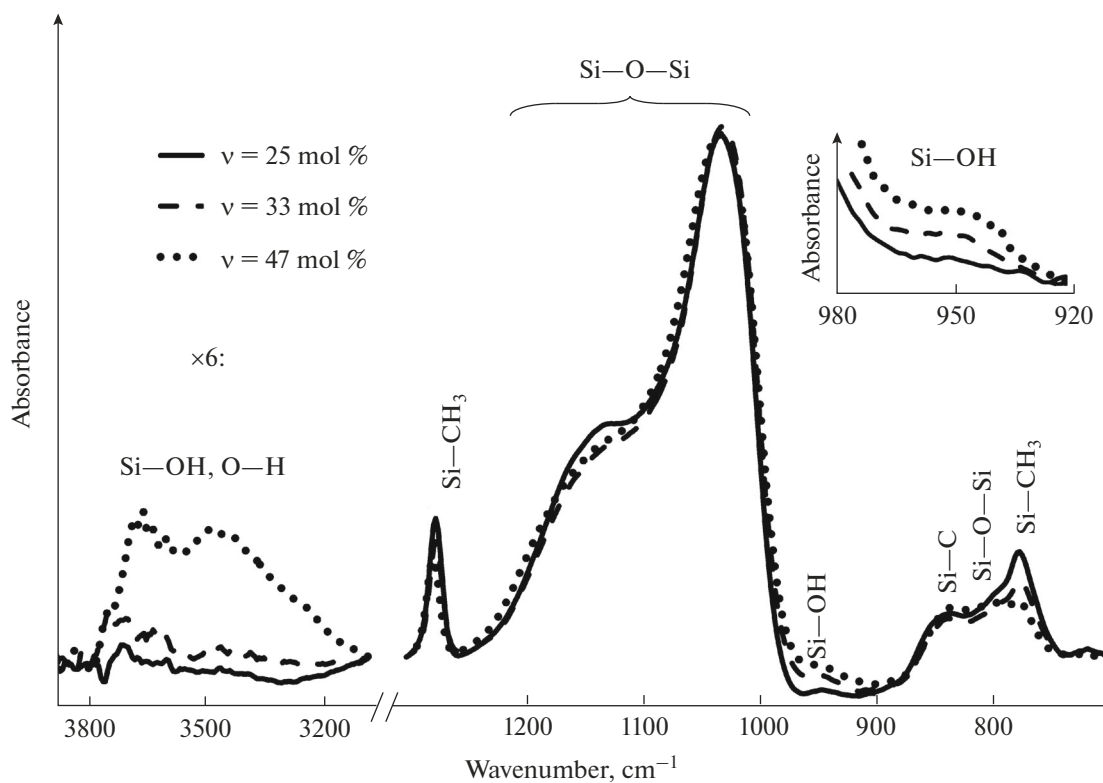


Fig. 2. IR spectra of the dense OAS films (BTMSE content $v = 25, 33,$ and 47 mol %; water : methoxy groups ratio $m = 0.6$) annealed at $t_a = 430^\circ\text{C}$. Inset: part of the IR spectra of the porous OAS films ($\omega_{\text{surf}} = 30$ wt %) annealed at $t_a = 430^\circ\text{C}$.

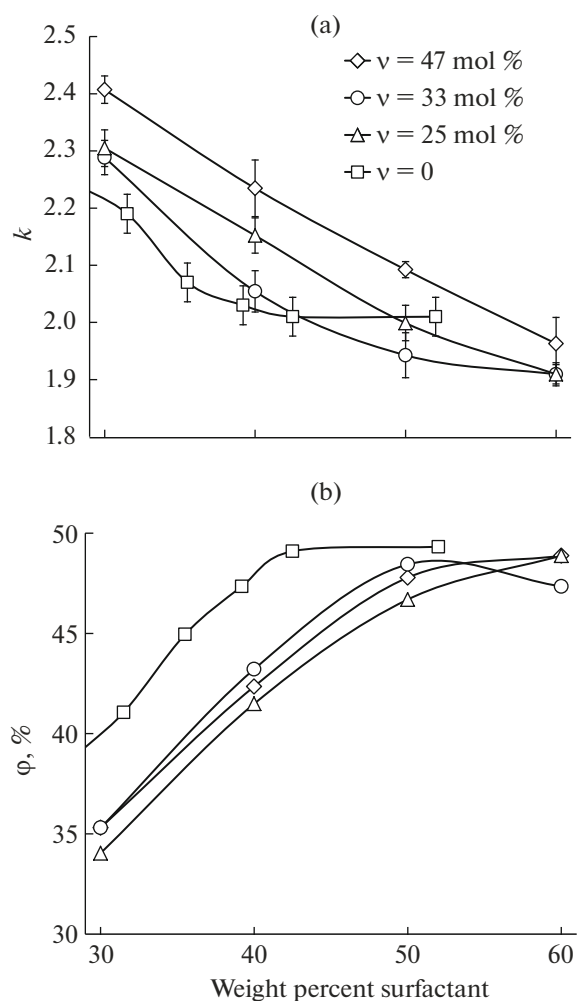


Fig. 3. (a) Dielectric permittivity k and (b) relative porosity ϕ as functions of surfactant content ω_{surf} for the porous OAS films ($v = 25, 33,$ and 47 mol % BTMSE; water : methoxy groups ratio $m = 0.6$) and PMSSQ films ($m = 0.7$) annealed at $t_a = 430^\circ\text{C}$.

The intensity of the Si–OH and O–H bands increases with an increase in the mole fraction of BTMSE in the dense and porous OAS films (Fig. 2 and the inset in it, respectively). The reason for this is that the cross-linking of the copolymer containing an increased amount of BTMSE large molecules is difficult to drive to completion. Similar behavior was observed by Kim et al. [5] and was found to cause an increase in k .

It is remarkable that increasing the fraction of BTMSE from 25 to 33% causes no marked broadening of the absorption band at 1127 cm^{-1} , in contrast to what is observed at a higher BTMSE content ($v = 47$ mol %). This may be due to more active formation of various Si–O–Si structure elements in the cage-like structure [16], different from the regular ladder-like structure of

PMSSQ [17], which agrees with previously reported data [18].

Figure 3 shows k and the relative porosity ϕ as functions of surfactant content for the porous films differing in BTMSE content. The $k(\omega_{\text{surf}})$ curve of the porous PMSSQ films has a characteristic saturation region due to the deficiency of silanol groups, which are responsible for the attachment of the surfactant [15, 19]. The k of the porous OAS films continues to decrease with increasing ω_{surf} (Fig. 3a) because, compared to the MTMS polymer, the MTMS–BTMSE copolymer in the film-forming solution has a larger number of silanol groups, which react with the added surfactant molecules owing to the increased degree of functionality of BTMSE. The relative porosity increases with increasing surfactant content (Fig. 3b). The lowest values of k are offered by the copolymer with $v = 33$ mol %, because it has the highest porosity, whereas the highest values of k are observed at $v = 47$ mol %, because of the high content of residual silanol groups, as shown above (Fig. 2).

It is worth noting that, even though the porosity of the OAS films remains essentially constant at surfactant concentrations in the range 50–60 wt % (Fig. 3b), the $k(\omega_{\text{surf}})$ curve continues to fall off (Fig. 3a). An increase in porosity in such systems is known to be accompanied by an increase in pore size (see, for example, Michalak et al. [20]). This leads to a reduction in k due to the associated decrease in specific surface area and, hence, in the number of silanol groups located on it and responsible for water sorption processes [2].

The effect of the water : methoxy groups ratio on the properties of the films was studied using the films with $v = 47$ mol % and $m = 0.5, 0.6,$ and 0.7 as an example. Figure 4 presents IR spectra of the dense films produced from film-forming solutions differing in water content, and Figs. 5a and 5b show k and the relative porosity ϕ as functions of surfactant content for the OAS films.

An increase in m leads to an increase in the amount of silanol groups at $t_a = 100^\circ\text{C}$ (Fig. 4, inset). At $t_a = 430^\circ\text{C}$, the absorption bands corresponding to Si–CH₃ vibrations remain unchanged (Fig. 4), suggesting that both precursors are involved in the copolymerization process.

The incomplete hydrolysis of the alkoxy groups at $m = 0.5$ leads to the formation of inherently weakly bonded OAS matrix skeleton, which experiences considerable shrinkage as a result of heat treatment (24% against 18 and 16% in the samples with $m = 0.6$ and $m = 0.7$, respectively) and forms a properly cross-linked structure, as evidenced by the shift of the Si–O–Si peak to higher wavenumbers (Fig. 4). The deficiency of silanol groups in such a film-forming solu-

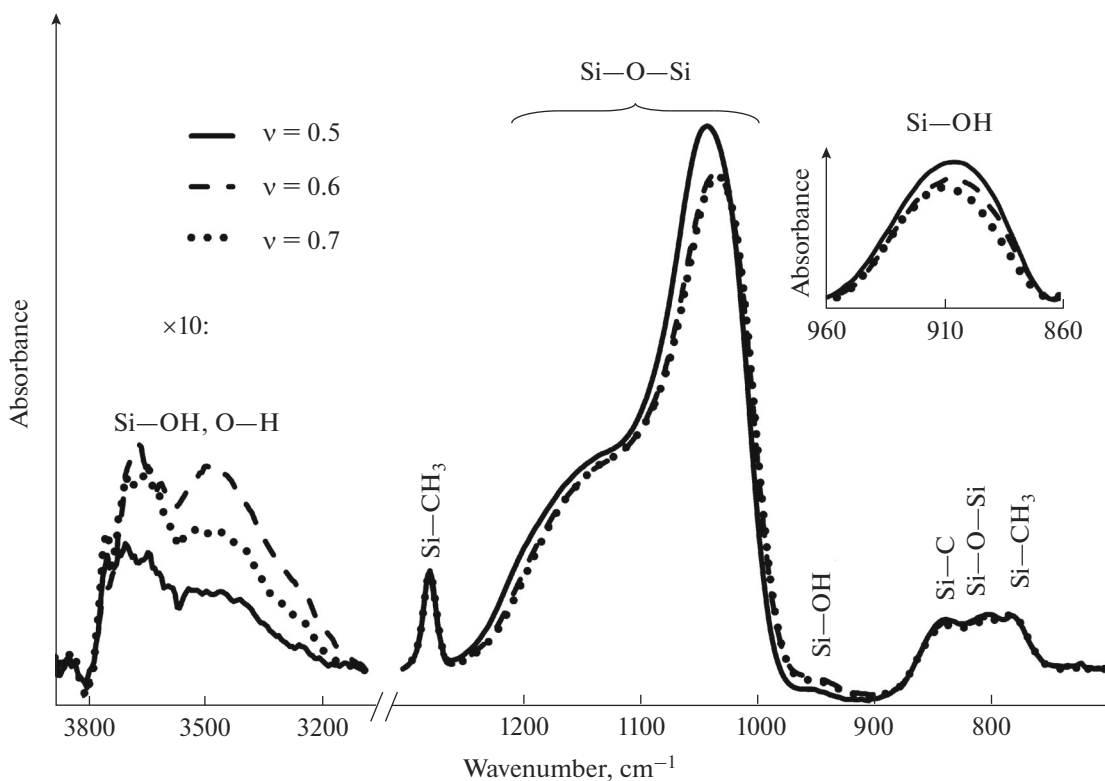


Fig. 4. IR spectra of the dense OAS films (BTMSE content $v = 47$ mol %; water : methoxy groups ratio $m = 0.5, 0.6,$ and 0.7) annealed at $t_a = 430^\circ\text{C}$. Inset: part of the IR spectra of the films heat-treated at $t_a = 100^\circ\text{C}$.

tion of the matrix copolymer leads to the lowest relative porosity values, with a characteristic saturation portion (Fig. 5b), and the highest k values (Fig. 5a).

At $m = 0.6$, the intensity of the Si-OH band increases owing to the uncondensed silanol groups of the BTMSE. At $m = 0.7$, it remains essentially unchanged (Fig. 4).

The increase in the content of silanol groups in the film-forming solution of the matrix polymer at $m > 0.5$ leads to a considerable increase in porosity, causing a reduction in k , in spite of the increased amount of residual silanols (Fig. 5).

CONCLUSIONS

We have prepared homogeneous stable film-forming solutions in which the cohydrolysis and cocondensation of the MTMS and BTMSE precursors (at different ratios between the precursors, $v = 0-47$ mol %) in the aprotic solvent THF in the presence of water (water : methoxy groups ratio $m = 0.5-0.7$) and HCl as a catalyst have been conducted. To obtain porous materials, the Brij 30 surfactant (concentration $\omega_{\text{surf}} = 30-60$ wt %) was added to the film-forming solution.

Homogeneous OAS films with a certain structure have been grown on single-crystal silicon substrates by

spin coating, using the film-forming solutions. Porous films have been produced via evaporation-induced self-assembly of surfactant micelles, whose hydrophilic part attaches to the polymer matrix by hydrogen bonds and which act as its structure-forming agent.

Subsequent destruction of the surfactant molecules in the polymer matrix, accompanied by the formation of a porous structure, has been ensured by two-step heat treatment (drying at $\approx 200^\circ\text{C}$ and annealing at $t_a = 430^\circ\text{C}$).

According to the present IR spectroscopy data, the addition of BTMSE to the film-forming solution leads to the breakdown of the regular ladder-like structure of PMSSQ and the presence of residual silanol groups in the OAS.

Spectral ellipsometry data indicate that the relative porosity ϕ is determined by the number of silanol groups in the film-forming solution of the matrix copolymer and depends on cohydrolysis conditions (water content, m). At $m = 0.5$, we have obtained the lowest ϕ values and the highest k values. Porosity as a function of surfactant content, $\phi(\omega_{\text{surf}})$, has a characteristic saturation region due to the deficiency of free silanol groups, which are responsible for the attachment of the surfactant molecules. At $m > 0.5$, the

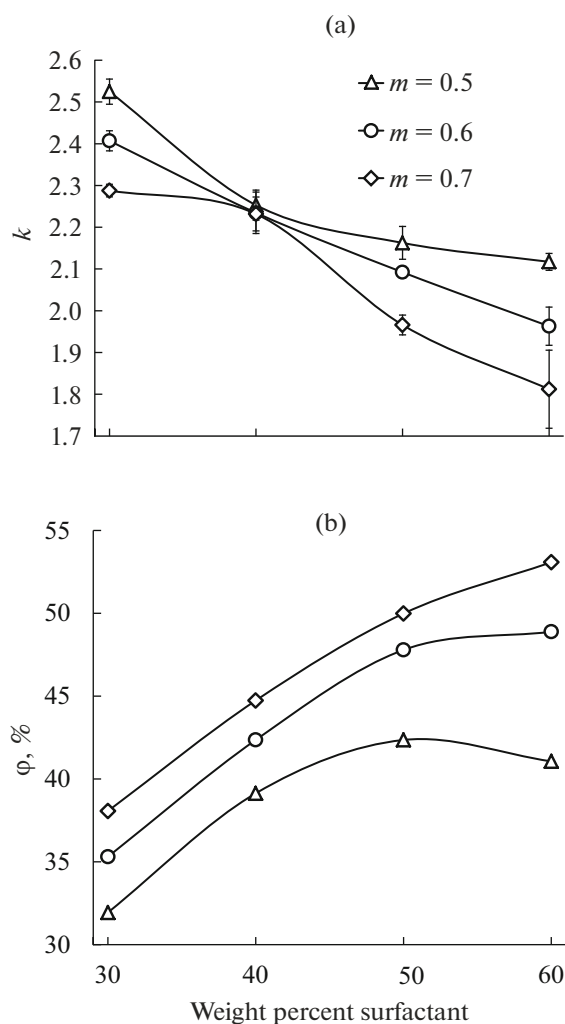


Fig. 5. (a) Dielectric permittivity k and (b) relative porosity ϕ as functions of surfactant content ω_{surf} for the porous OAS films ($v = 47$ mol % BTMSE; water : methoxy groups ratio $m = 0.5, 0.6,$ and 0.7) annealed at $t_a = 430^\circ\text{C}$.

increase in the content of silanol groups leads to an increase in ϕ and, as a consequence, to a decrease in k .

The present results demonstrate that the samples with a relative porosity of 38% prepared from the film-forming solution containing 47 mol % BTMSE ($m = 0.7$) and 30 wt % surfactant have $k \approx 2.3$ and are potentially attractive materials for use as insulators in integrated circuits.

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