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Stability of low-*k* organosilicate dielectrics with benzene bridges to vacuum ultraviolet plasma radiation during Ta barrier layer deposition

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The stability of low-k periodic mesoporous organosilicate low-*k* dielectrics with benzene bridges to VUV plasma radiation during the deposition of tantalum barrier layers by magnetron sputtering with additional ionization by inductively coupled plasma has been studied. The correlation of composition and porous structural features of the samples with their hydrophobicity and resistance to VUV was found.

Keywords: low low-*k* dielectrics, VUV, barrier layers, PVD.

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Porous organosilicate glasses (OSG) with low dielectric permittivity (low-*k*) are used in microelectronics for ultra large-scale integration (ULSI) circuits. The reduction of the dielectric permittivity k is achieved by introduction of terminal carbon groups into the matrix SiO_2, which results in formation of bonds with lower polarity Si–C (versus Si–O) and the emergence of micropores. The porosity can be increased by adding a removable organic porogen [1]. The porosity decreases k, however, it decreases mechanical strength of dielectrics as well [2]. Introduction of organic bridge groups into the matrix SiO_2 instead of the bonds ≡Si–O–Si≡ increases the material strength, reduces its density and k [3]. The embodiment is periodic mesoporous organosilicate (PMO) materials [4]. The mechanical strength and controllable porosity make PMO films potentially promising as interlayer dielectrics for microelectronics.

A dielectric material must withhold the exposure to plasma in damascene-process of integration of copper interconnects [5]. In order to prevent the diffusion, copper interconnects are separated from the dielectric by a barrier layer (usually made of Ta or TaN), formed by physical vapor deposition with additional ionization of the flux of sputtered atoms (IPVD). The exposure of OSG dielectric to plasma leads to its damage by active radicals, ions of plasma and vacuum ultraviolet (VUV) radiation [6]. Usually, the damage is caused by the removal of methyl groups ensuring the hydrophobic properties of the material, which results in increase of k.

In the present work we studied the resistance of PMO films with benzene bridges to VUV radiation of IPVD plasma in the conditions of the barrier layer deposition. Among carbon bridges the benzene ones are less studied compared to the others, though these are more interesting because of the best mechanical properties due to formation of a quasi-crystalline matrix [7]. The disadvantage of these materials is hydrophilic properties leading to increase in k (as shown in Table). To solve that problem one adds terminal methyl groups; meanwhile the change of mechanical characteristics is of a percolation nature, which is associated with difficulties in forming a quasi-crystalline skeleton in the presence of such groups. This is why when selecting the like materials for using in the ULSI manufacture process one need to study other properties of that family of materials near to the percolation threshold.

Two types of films were produced. The first one — methyl-modified silicates, in which the bonds ≡Si–O–Si≡ are partially replaced with bridge benzene groups $\equiv Si{-}C_6H_4{-}Si\equiv$, obtained by cohydrolysis of methyltrimethoxysilane (MTMS) and 1.4-Bis(triethoxysilyl)benzene (BTESB) in tetrahydrofurane (PMO films) [7]. The second one — methyl-modified silicates obtained by cohydrolysis of tetraethoxysilane (TEOS) and methyltetraethoxysilane (MTEOS) in water-alcohol medium (OSG films) [8]. The films were deposited on Si (100) substrates (Ø 100 mm) by centrifugation with further heat treatment in the air (200°C, 30 min) and in nitrogen (430°C, 30 min). The effective porosity and pore distributions by radius were assessed by means of ellipsometric porosimetry. The applied methods of determination of the parameters of films are described in [9]. The composition calculated from the ratio of precursors represented as the ratios of concentrations $[CH_3]/[Si]$, $[C_6H_4]/[Si]$, $[O]/[Si]$, and the measured characteristics of the produced dielectrics are given in Table (hereinafter square brackets denote the concentrations). The samples with „p“ prefix were obtained by adding a porogen Brij® L4 ($C_{12}H_{25}(OCH_2CH_2)_4OH$) in the amount of 19.4 or 30 wt.% for OSG and PMO respectively, and with the „d“ prefix — without the porogen.

Characteristics of pristine dielectric films (d and n — thickness and refraction index, V_{open} and S — effective porosity and specific surface area according to the data of ellipsometric porosimetry)

Sample	Molar ratio of precursors in film-forming solution	$[CH_3]/[Si]$	$[C_6H_4]/[Si]$	$[O]/[Si]$	d, nm (±3)	n (±0.001)	k (±0.1)	V_{open}, % (±1)	S, m^2/cm^3
d100	BTESB/MTMS=100/0	0	0.5	1.5	215	1.50	16.3	5	255
p100	BTESB/MTMS=100/0	0	0.5	1.5	213	1.38	5.2	26	914
p45	BTESB/MTMS=45/55	0.38	0.31	1.5	258	1.30	2.6	38	765
p25	BTESB/MTMS=25/75	0.6	0.2	1.5	204	1.30	2.3	37	559
pOSG	TEOS/MTEOS=40/60	0.6	–	1.7	181	1.26	2.3	36	427
dOSG	TEOS/MTEOS=40/60	0.6	–	1.7	219	1.38	3.0	9	219

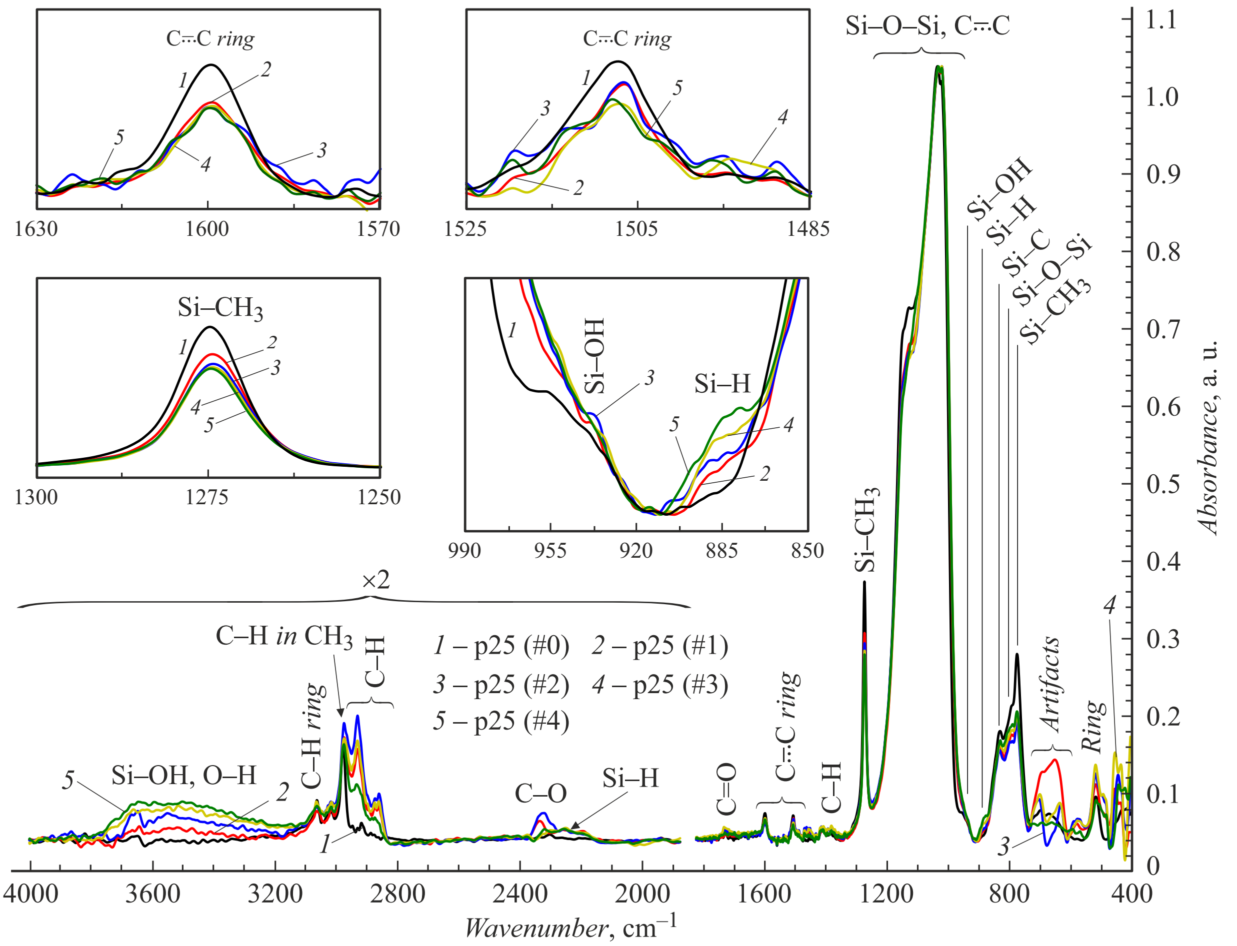

Figure 1. An example of IR spectra of p25 samples after exposure to IPVD plasma in different regimes (#0, #1, #2, #3, and #4). The spectra are normalized to the maximum of the superposition of the Si–O–Si band and the C=C peaks of benzene ring.

Magnetron sputtering of tantalum barrier layers was performed in a vacuum IPVD chamber equipped with a carousel holder for substrates, which enabled one-by-one coating deposition on the groups of several substrates 12 × 12 mm. Before the experiment begins, the samples were heated under vacuum conditions for at least 20 min at the temperature of 200–230°C to remove the adsorbed water; a tantalum target was closed with a shutter and was sputtered in advance to remove the oxide layer. For minimizing the effect of plasma ions, the holder was under floating potential of about 8 V, and the plasma potenrial was 16–19 V. The experiment setup is described in details in [9].

The samples were subjected to IPVD-discharge plasma exposure in various regimes within the time (t) required for deposition of the 5 nm coating under pressure of working gas (argon) 35 mTorr:

#0 — pristine samples;

#1 — $P_{\mathrm{ICP}} = 50\,\mathrm{W}$, $I_M = 0.3\,\mathrm{A}$, $t = 357\,\mathrm{s}$;
#2 — $P_{\mathrm{ICP}} = 150\,\mathrm{W}$, $I_M = 0.3\,\mathrm{A}$, $t = 329\,\mathrm{s}$;
#3 — $P_{\mathrm{ICP}} = 300\,\mathrm{W}$, $I_M = 0.3\,\mathrm{A}$, $t = 329\,\mathrm{s}$;
#4 — $P_{\mathrm{ICP}} = 300\,\mathrm{W}$, $I_M = 0\,\mathrm{A}$, $t = 329\,\mathrm{s}$.

Here P_{ICP} — the power of inductive radio-frequency discharge, I_M — the magnetron discharge current. The dependence of t on P_{ICP} is explained by the gas heating. The analysis of chips of silica substrates by means of scanning electron microscopy showed the uniformity of thickness of the coatings deposited on them. In the regime #4 no coating was deposited ($I_M = 0\,\mathrm{A}$), however, a small tantalum deposition was possible as a result of weak sputtering of ICP inductor being under the self-bias potential $-45\,\mathrm{V}$. Chemical composition and structure of low-*k* films before and after treatment were studied by the IR-spectroscopy (Fig. 1).

Since the ions energy is low, the main damage to the dielectrics is caused by the loss of hydrophobic properties as a result of tearing off the terminal groups $\mathrm{Si{-}CH_3}$ under exposure to VUV radiation of atoms (104.8 and 106.7 nm) and ions (92.0 and 93.2 nm) of argon [9], which is characterized by the increase of the intensity of the band Si–OH, OH ($3700{-}3000\,\mathrm{cm^{-1}}$). Fig. 2, *a* shows concentration [Si–OH, OH] in the samples (ratio of the area of corresponding peak or band to the value d as adjusted for V_{open}). High concentration [Si–OH, OH] in the samples p100 and d100 and its reduction during plasma treatment indicate that the double-stage heat treatment appeared to be insufficient for them, and the curing process continued under exposure to UV-radiation of plasma. However, higher values [Si–OH, OH] for the treatment #4, versus that for the treatment #3, indicate that the minimum values have already been reached and further decrease is impossible due to a competing process of destruction of the groups $\equiv\mathrm{Si{-}C_6H_4{-}Si}\equiv$, resulting in generation of silanol groups that adsorb water. The reason could be virtually total absence of Ta-coating that partially protects the film from VUV radiation, in the regime #4 ($I_M = 0$). Peaks $\mathrm{Si{-}CH_3} \sim 1275\,\mathrm{cm^{-1}}$ are present in spectra of all samples, except for p100 and d100, for which there is a weak band consisting of the sum of the peaks is observed, which is indicated by its unusually large width and non-symmetry.

Fig. 3 shows examples of pore distributions by radius in the samples. The increase in BTESB concentration correlates with the decrease in the pore radius, which makes films better fitting for the deposition of thin barrier coatings on them [10], meanwhile increasing the specific surface area (see Table). As a result, the number of methyl groups located on the pores surface could appear to be insufficient for provision of hydrophobic properties of the film. An optimum content of BTESB is reached in the sample p25. Compared to the sample pOSG, which is similar to those used in microelectronics, the pristine p25 has a lower radius of pores and the same well hydrophobic properties, ensured by a high content of methyl groups ($[\mathrm{Si{-}CH_3}]/[\mathrm{Si}]=0.6$ in p25 and pOSG, see Table). At the same time, the losses of methyl groups under exposure to VUV radiation in p25 appear to be lower than in pOSG (Fig. 2, *b*), which can be explained by efficient absorption of radiation by benzene bridge structures of the sample p25 [10]. The BTESB content in p45 is higher than in p25; therefore, relative losses of methyl groups are even lower. However, hydrophobic properties of the pristine sample (characterized in the content of [Si–OH, OH]) appears to be worse than that of p25 and pOSG, which can be explained by higher specific area of the pores surface and lower value of $[\mathrm{Si{-}CH_3}]/[\mathrm{Si}]=0.38$. Nevertheless, because of a high resistance to VUV radiation, hydrophobic properties of p45 after exposure to plasma in all regimes appear to be better than that of pOSG, but worse than that of p25.

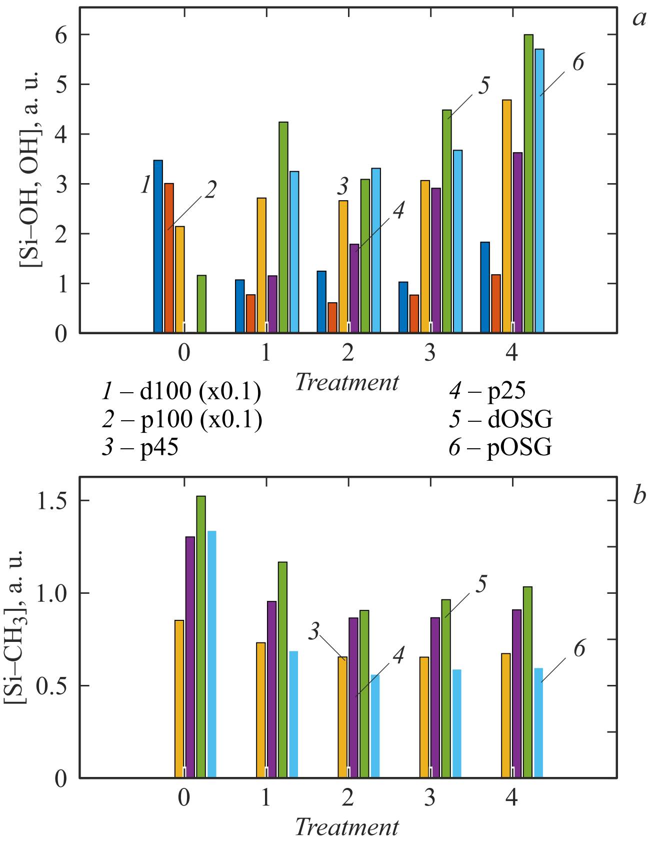

Figure 2. The content of [Si–OH, OH] (*a*) and $[\mathrm{Si{-}CH_3}]$ (*b*) in the samples after exposure to IPVD-discharge plasma in various regimes (#0, #1, #2, #3 and #4). The values for d100 and p100 on the part *a* were decreased 10 times.

Thus, the study has demonstrated that the increase in the BTESB concentration in the sample of low-*k* films contributes into decreasing the pores radius and increasing the resistance to VUV radiation. However, accompanying

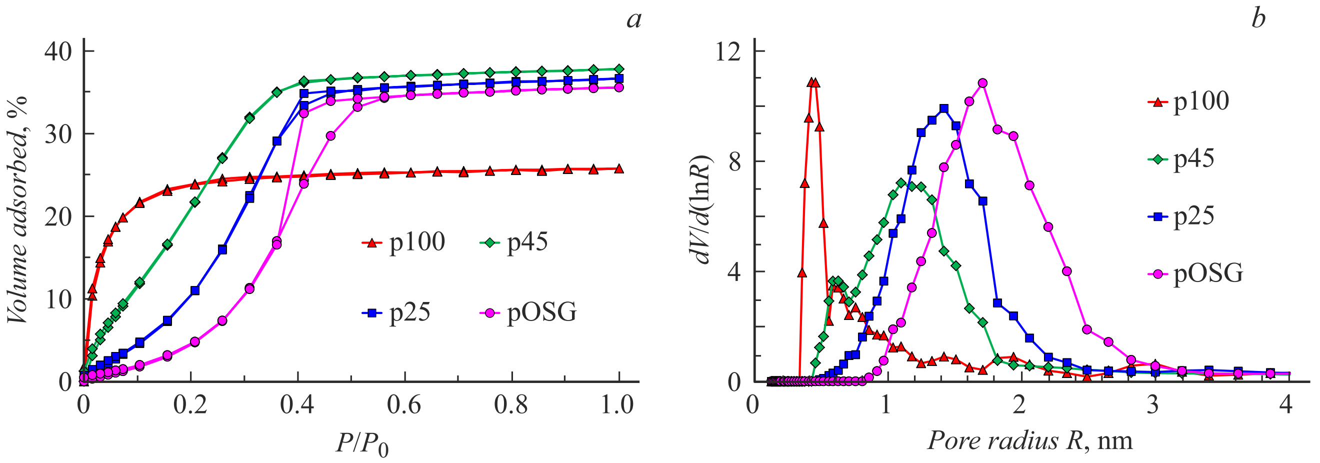

Figure 3. *a* — adsorption and desorption isotherms obtained by ellipsometric porosimetry under atmospheric pressure. *b* — pore distribution by radius in the pristine samples of films with porogen addition, calculated by using the adsorption curves. Isopropyl alcohol was used as the probe molecules.

decrease of the number of bonds Si$-$CH$_3$ and rise of the specific area of the pores surface could lead to decrease in hydrophobic properties. With an optimum BTESB content, the characteristics of the produced PMO film were improved compared to the characteristics of a conventional OSG used in the ULSI production.

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Conflict of interest

The authors declare that they have no conflict of interest.

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