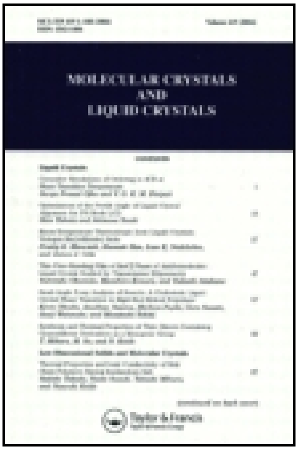

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New Hydrophobic Microporous Dielectric Films Made on the Basis of the CTAB/TSC-2/TEOS Precursor Solution

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We propose a method to form new solid, silicon-containing, substrate-supported films with low moisture absorption. These films may be used in microelectronics as low dielectric constant interlayers. Such films are made utilizing a precursor solution containing cethyltrimethylammonium bromide (CTAB) surfactant (as a porogene template) dissolved in a mixture of butanol and water with the addition of silicon-containing materials tetraethyl orthosilicate (TEOS) and polyfunctional silaxane network precursor (TCS-2). TSC-2 considerably decreases the films' water absorption. To make films even more hydrophobic, they are subject to supplementary treatment (after calcination) with hexamethyldisilizane (HMDS) (in stirring bulk or by spin-coating) and to heating up to 420°C in a vacuum furnace. The obtained films demonstrate lower atmospheric water absorption and, hence, lower values of dielectric constant (around 3) than other surfactant-based, silicon-containing films (e.g., CTAB/sodium salicylate (NaSal)/TEOS).

Keywords: calcination; low-*k* materials; nanoindentation; precursor solution

INTRODUCTION

Materials with low dielectric constant (the so-called low-*k* materials) are widely used in electronics (e.g., Ref. [1]). The application of such substances as dielectric interlayers in electronic chips makes it

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possible to increase considerably the speed of propagation of electric signals and to reduce dielectric losses.

The low-k materials, first, must have the lowest possible values of dielectric constant and, second, exhibit considerable mechanical strength in order to withstand severe conditions of exploitation.

The first condition is fulfilled by adding into such materials some fraction of air (having $k = 1$) in the form of pores. Obviously, to get lower value of k, one needs to have a larger volume fraction of such pores in the low-k substance.

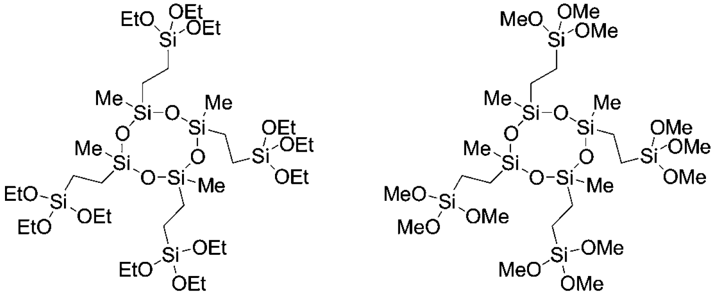
The second condition may be achieved by spatial (crystalline) ordering of pores. The so-called “liquid crystal templating” technique (e.g., Refs. [2–4]) is the most commonly used method for fabrication of the low-k materials with ordered pores.

Moisture absorption from the atmosphere considerably damages the quality of porous dielectric films, especially silicon-containing ones. Indeed, absorbed water noticeably increases the dielectric constant of such films. To prevent water absorption, antiabsorption treatment procedures can be used:

1. Complex treatment of dielectric films with chemicals [such as hexamethyldisilizane (HMDS) and trimethylchlorosilane (TMCS)], making the film surface hydrophobic, together with heating the film to temperatures around 400°C in flowing gas mixtures (such as H_2-N_2 and Ar) to evaporate already absorbed water [5].
2. Film cleaning by means of supercritical CO_2, in which HMDS or TMSC is dissolved [6–9].
3. Potential use of the Ar-N_2 cryogenic aerosols for cleaning dielectric films from the absorbed water [10,11].
4. Insertion of some hydrophobic molecular fragments (e.g., F in SiOF dielectric films [12]) or hydrophobic components into the film material structure.

Good candidates for the hydrophobic components for use in dielectric films (method 4) are polyfunctional silaxane network precursors TSC-2 (both with methylic or ethylic end groups) (Fig. 1), employed in [13] and named there as “1.” These substances are expected to make dielectric film strongly hydrophobic and, thus, lower its dielectric constant.

In Ref. [13], a solid powder was prepared on the basis of the following precursor solution: cethyltrimethylammonium bromide (CTAB)/tetraethyl orthosilicate (TEOS)/TSC-2/water/HCl. It was shown that this powder possessed micropores with an average diameter of 1.8 nm. However, neither dielectric nor mechanical properties of this new material were studied.



$C_{36}H_{88}O_{16}Si_8$
Mol. Wt.: 1001.76

TCS-2(C_2H_5OH)

$C_{24}H_{64}O_{16}Si_8$
Mol. Wt.: 833.44

TCS-2(CH_3OH)

FIGURE 1 Structural chemical formulas of TSC-2 substances.

Note that, in most cases, any of these four treatment procedures, taken alone, does not give stable, low values of *k* for dielectric films. Thus, in this work, we combined methods 1 and 4 to obtain Si substrate-supported dielectric films, having stable, low values of *k* and high mechanical properties.

METHODOLOGY

Following Ref. [13], we also utilized TSC-2 in our precursor solution but altered the solvent (a mixture of butanol and water was used instead of pure water). The reason for this change was the low solubility of TCS-2 in water.

The following optimal procedure for fabrication of precursor solution was elaborated:

1. The CTAB-based porogene-templating (25 mM/l) solution in a butanol–water mixture (22:5 by molar ratio) was prepared and kept at room temperature for 1 day in order to attain a thermodynamic equilibrium.
2. TEOS (1 M/l), TCS-2 (with ethylic end groups, see Fig. 1) (50 mM/l), and 35% HCl (0.1 M) were added into this solution, and mixture was stirred.

Solid dielectric films were made as following.

1. The final CTAB/TEOS precursor solution was spin-coated in one or several layers (with soft for 1 min at 150°C and hard for 1 min at

250°C to bake each layer) on Si or Si + (Ti + Al) electrode wafers at 3000 rpm. The thickness of one layer was approximately 400 nm.

2. The obtained films were calcinated in a vacuum furnace for several hours at 450°C to burn out the organic material (CTAB) and to produce pores.

We had found that to stop the process of the film preparation at stage 2 was not sufficient. Indeed, notwithstanding the fact that the presence of TSC-2 in the film considerably decreased the moisture absorption, some water was still captured inside. This circumstance did not allow us to reach stable, low-enough values of k.

Thus, additional antimoisture-absorption treatment was employed. The films were treated for 24 h in stirring HMDS (or HMDS was directly spin-coated on the film surface) and, further on, the films were heated for 1 h in a vacuum furnace at 420°C (method 1, see Introduction).

In the course of this treatment HMDS reacted with silicon-containing material of the film. As a result of this chemical reaction, hydrophilic $Si{-}OH$ bonds of the film were replaced by hydrophobic $Si{-}O{-}Si(CH_3)_3$ bonds. This made the film hydrophobic and lowered its dielectric constant.

As a result, Si wafer-supported hydrophobic dielectric films with stable, low values of k were produced.

We describe results of our investigations of the structure and physical properties of the obtained films next.

EXPERIMENTS AND RESULTS

Structure

To investigate our CTAB/TEOS/TSC-2 film structure, we used transmission electron microscopy (TEM).

Figure 2 shows three TEM images of the monolayer films. The first image (Fig. 2a) reflects the structure of the non-antiabsorption-treated (no HMDS) film. The second one (Fig. 2b) represents periodic, thread-like, most probably carbon-containing, structures at the surface of the non-antiabsorption-treated film. The third image (Fig. 2c) shows the film after treatment for 24 h in stirring HMDS with further 420°C heating.

The structure of all studied films is amorphous. The films, most probably, contain randomly distributed micropores 1–2 nm in diameter.

Mechanical Properties

Figure 3 shows our nanoindentation data for Young's modulus (curve 1) and hardness (curve 2) obtained for the bilayer

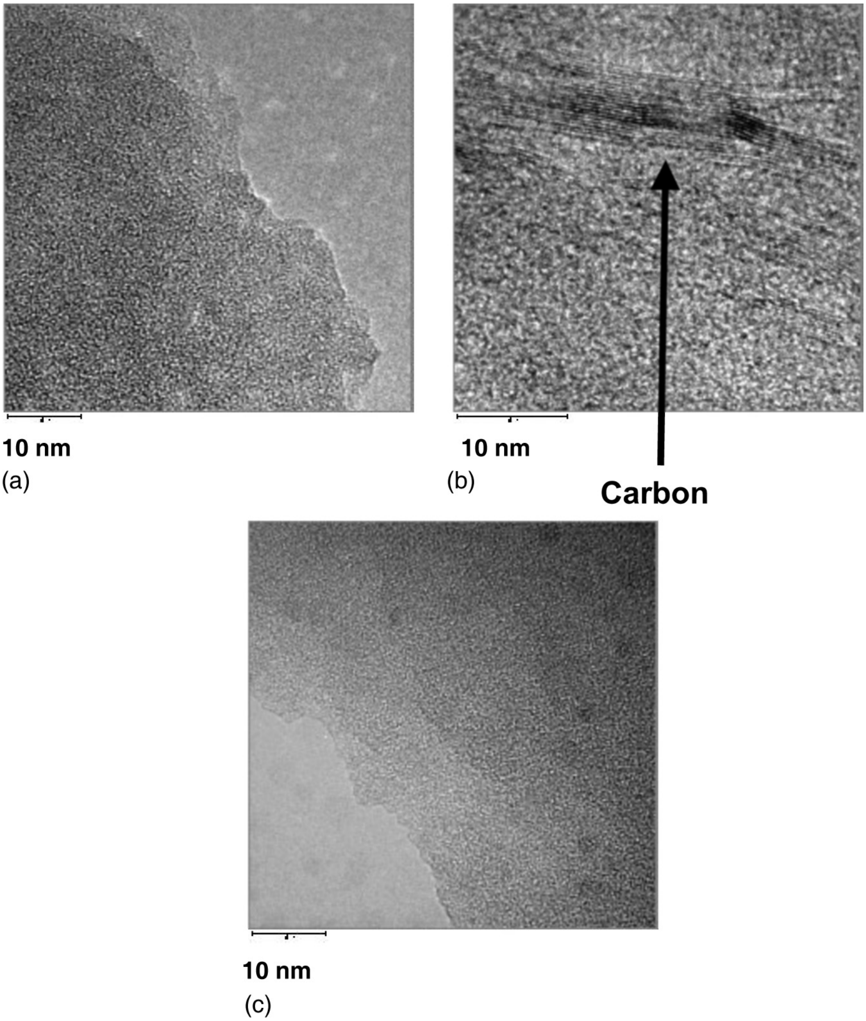


FIGURE 2 TEM images of the Si wafer-supported CTAB/TEOS/TSC-2 film: (a) and (b) non-antiabsorption-treated films, and (c) film treated for 24 h in stirring HMDS and heated in vacuum furnace for 1 h up to 420°C. All films contain randomly distributed micropores. Film (b) exhibits, in addition, carbon thread-like inclusions.

CTAB/TEOS/TSC-2 non-antiabsorption-treated film (a) and film treated for 24 h in stirring HMDS and heated to 420°C (b). Film (a) has minimal values of the two parameters 7.2 and 0.9 Gpa, whereas the same parameters for film (b) are almost two times higher—13.0

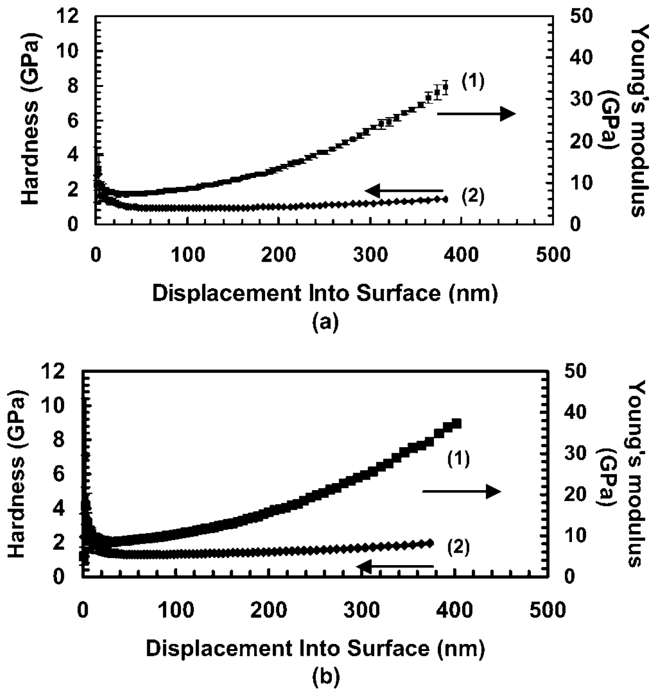


FIGURE 3 Nanoindentation data on Young's module (curve 1) and hardness (curve 2) for the CTAB/TEOS/TCS-2 Si wafer-supported films. (a) non-antiabsorption-treated film and (b) film treated for 24 h in stirring HMDS and heated in a vacuum furnace for 1 h up to 420°C.

and 1.8 Gpa. This means that the antiabsorption treatment considerably increases mechanical properties of dielectric films.

This can be explained as follows. The Si–O–Si$(CH_3)_3$ bonds in film (b) are stronger than the Si–OH bonds in film (a). The latter bonds have tendency to decompose under the action of air, heat, and radiation. Thus, the HMDS-treated film (b) (with Si–O–Si$(CH_3)_3$ bonds) should exhibit stronger mechanical properties.

Note, however, that for the higher water-absorbing system CTAB/NaSal/TEOS, with polycrystalline ordering of cylindrical pores, mechanical properties are even stronger: minimal Young's modulus is 29.6 Gpa and minimal hardness is 2.7 Gpa [14].

Dielectric Constants

Dielectric constant *k* of our bilayer films was measured by means of the capacitance method for the frequency of the applied voltage

TABLE 1 CTAB/TEOS/TSC-2 Films' Dielectric Constant Values for Different Temperatures

Dielectric film	Temperature,°C	Dielectric constant, *k*
Non-antiabsorption-treated film (a)	25	6.6
	150	3.6
	200	3.4
Antiabsorption-treated film (b)	25	3.8
	150	3.2
	200	3.1

$f = 100\,\text{kHz}$ using a special furnace table for heating. Film thickness was estimated by means of the profiler, or, together with the refractive indices, by the prism coupler.

The obtained data on *k* for films (a) and (b) (see previous paragraph) measured at different temperatures are represented in Table 1. For both films *k* diminishes with the growing temperature. Dielectric constants for both films have quite low values at 200°C: 3.4 for film (a) and 3.1 for film (b). At room temperature *k* is not small and not stable (gradually growing with time) for film (a), whereas it is stable with time (does not change its value for many days) and has a quite low value (3.8) for film (b). It means that our antiabsorption treatment of dielectric films diminishes the *k* value and improves its time stability.

CONCLUSION

We have fabricated novel CTAB/TEOS/TSC-2-based Si substrate-supported microporous films having strong mechanical properties and low value of the dielectric constant. It is shown than an antiabsorption treatment of these films with HMDS improves their mechanical properties and decreases their dielectric constants making it stable in time.

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