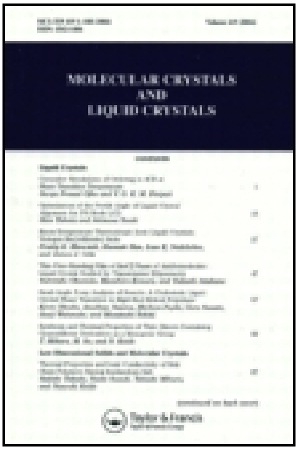

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Use of Supercritical CO_2 for Preparation of Novel Microporous CTAB/TCS-2/TEOS-Based Dielectric Films

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We developed a novel cethyltrimethylammonium bromide (CTAB)/commercial name (polyfunctional silaxane network precursor) (TSC-2)/tetraethyl orthosilicate (TEOS)-based precursor solution for the preparation of low-dielectric-constant materials. Thin, solid dielectric films were fabricated by spin-coating this precursor solution on silicon wafers and drying and calcinating the obtained layers. TSC-2 considerably lowered atmospheric water absorption by dielectric films and, hence, their dielectric constant. Additional treatment of dielectric films by the hexamethyldysilizane (HMDS) solution in supercritical CO_2 *effectively decreased moisture absorption by the film, making its dielectric constant even lower and stable over time. This treatment also made the film mechanical modulus higher.*

Keywords: Calcination; Low-*k* materials; Nanoindentation; Precursor solution; Supercritical CO_2

INTRODUCTION

Materials with low dielectric constant k (the so-called low-k materials) have potential for application in the electronic industry (e.g., [1]). The

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use of substances such as dielectric interlayers in electronic chips makes it possible to considerably increase the speed of propagation of electric impulses and to reduce dielectric losses.

The most essential requirements of the low-k materials are the following.

First, they must have the lowest possible dielectric constant values. Second, they must exhibit considerable mechanical strength in order to withstand severe conditions.

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

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

When this technique is used, an organic lyotropic liquid-crystalline phase, built by micelles or polymer chains, serves as a template for further formation of a solid low-k material. First, a mixture of an inorganic dielectric substance (e.g., some silicon-containing compound) with a lyotropic phase is prepared. In this mixture (usually called a "precursor solution"), the inorganic material occupies the continuous solvent region and, in the course of reaction of hydrolysis (e.g., [5]), forms inorganic walls between micelles or polymer chains. This is the so-called self-assembly (e.g., [6]) of surfactant (polymer) and silicon-containing material in the bulk of a solvent.

Thin solid films for electronic applications can be fabricated by depositing the precursor solution onto silicon wafers by spin- or dip-coating.

Further, the organic material is removed by calcinations: heating in a vacuum furnace up to several hundred degrees Celsius temperatures.

As a result, a sieve (a bulk sample or a film) with spatially ordered pores (having a controlled pore diameter of the order of several nanometers corresponding to diameter of micelles or polymer chains) is formed.

Note that in the most recent practice, isotropic (dilute) surfactant- or polymer-based solutions are often used as templates for preparation of low-k films (see, e.g., [7]). These solutions should contain supramolecular aggregates with prolonged form (cylindrical micelles, polymer chains). When deposited from solutions on solid surfaces, such aggregates normally form multidomain (or polycrystalline) structures with unidirectional alignment of aggregate long axes inside each domain. The use of dilute solutions is determined by practical purposes.

Indeed, such solutions are less viscous than liquid-crystalline ones and, hence, can be easily spin-coated on solid substrates.

An important problem that arises in the process of fabrication of the substrate-supported silicon-containing porous dielectric films is the absorption of water from an atmosphere. Moisture absorption considerably damages the quality of dielectric films. In particular, absorbed water noticeably increases the dielectric constant of such films.

Some methods, currently used to prevent moisture absorption, are outlined next.

First is a complex treatment of dielectric films with chemicals (the so-called hydrophobizing agents such as hexamethyldisilizane (HMDS) and trimethylchlorosilane (TMCS), which makes the film's surface hydrophobic, together with the films heating to the temperatures around 400°C in flowing gas mixtures (e.g., H_2-N_2, Ar), in order to evaporate already absorbed water (e.g., [8,9]).

Second is the potential use of the $Ar-N_2$ cryogenic aerosols for cleaning dielectric films from the absorbed water (e.g., [10,11]).

Third is the insertion of some hydrophobic molecular fragments (e.g., F, in SiOF dielectric films [12]) or hydrophobic components into the film material structure.

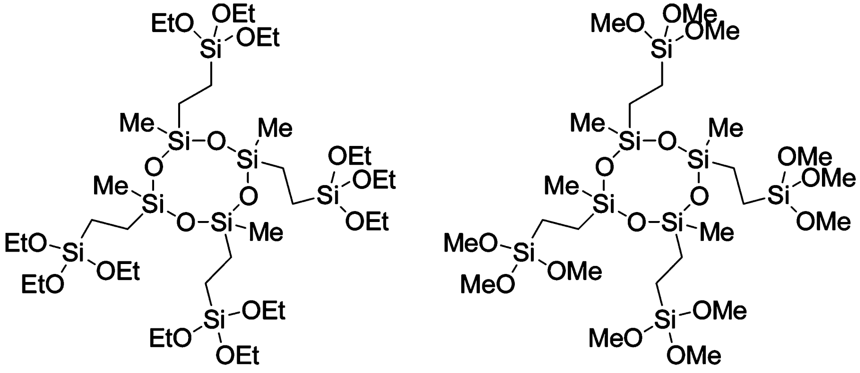
Fourth is a novel and quite perspective technique: film treatment by the supercritical CO_2 ($SC-CO_2$), in which HMDS or TMSC are dissolved (see, e.g., [13–16]). The use of the superfluid $SC-CO_2$ as a solvent allows a perfect transport of hydrophobizing agents in a porous medium.

The purpose of this work was to create highly hydrophobic silicon-containing dielectric films with low values of k and reliable mechanical properties using a simple and effective anti-absorption treatment. To achieve this, we had combined methods 3 and 4. We used a silicon-containing substance with hydrophobic molecular fragments as well as treatment with the hydrophobizing agent solution in the $SC-CO_2$.

METHODOLOGY

Our precursor solution contained a hydrophobic component—the polyfunctional silaxane network precursors, TSC-2, employed in Ref. [17] and named there as "1" (see Fig. 1). These substances are expected to make a dielectric film strongly hydrophobic and thus to lower its dielectric constant.

A solid powder was prepared in Ref. [17] on the basis of the following precursor solution: cethyltrimethylammonium bromide,



$C_{36}H_{88}O_{16}Si_8$
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.

$CH_3(CH_2)_{15}$–$(CH_3)_3N^+$–Br^- (CTAB)/TSC-2/TEOS/water/HCl. Here TEOS is tetraethyl orthosilicate, and $Si(OC_2H_5)_4$ is the silicon-containing material.

This powder possessed micropores with an average diameter of 1.8 nm. However, neither dielectric nor mechanical properties of this new material were studied.

We also used the CTAB/TCS-2/TEOS precursor solution. To improve the solubility of TCS-2, we utilized a mixture of butanol and water as a solvent instead of pure water, used in Ref. [17].

We developed the following optimal procedure for fabrication of the precursor solution.

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 to attain 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 the mixture was stirred.

Solid dielectric films were made as follows.

1. The resulting precursor solution (see previous steps 1 and 2) was spin-coated in one or several layers (with soft being 1 min at 150°C and hard being 1 min at 250°C baking of each layer) on Si

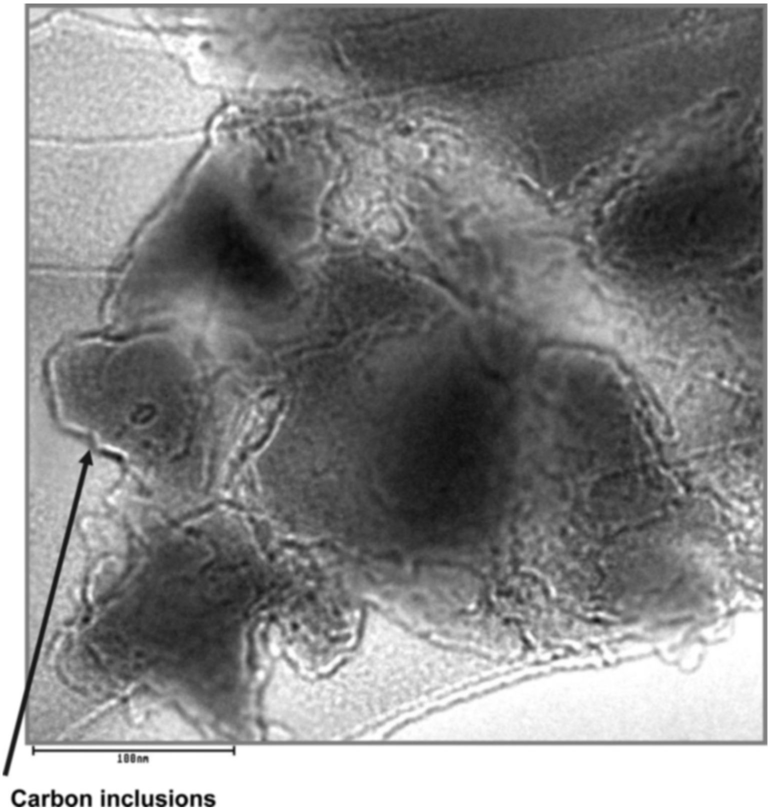


FIGURE 2 TEM images of the Si-wafer-supported CTAB/TEOS/TSC-2 film treated for 3 min with the mixture of SC$-$CO$_2$ and HMDS (1%). The film contains randomly distributed micropores and carbon thread-like inclusions (shown by an arrow).

or Si + (Ti + Al) electrode wafers at 3000 rpm. The thickness of one layer was approximately 350–400 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 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 enough low values of k. Thus, additional antimoisture absorption treatment, described as step 3, was needed.

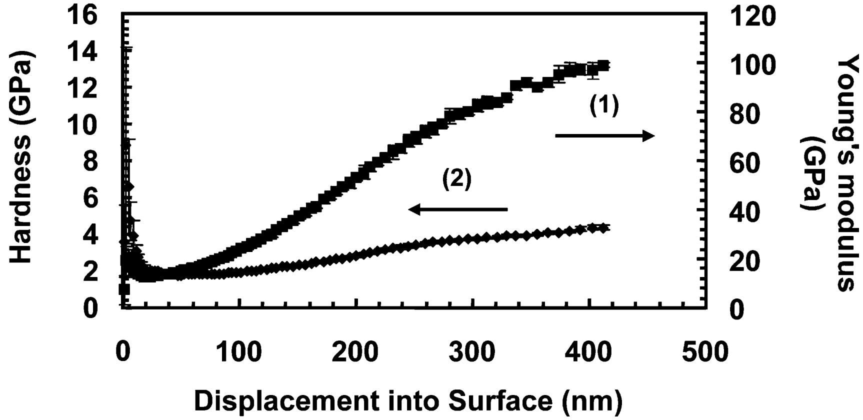


FIGURE 3 Nanoindentation data on Young's module (curve 1) and hardness (curve 2) for the CTAB/TEOS/TCS-2 Si-wafer-supported film treated for 3 min by the mixture of SC−CO_2 and HMDS (1%).

3. The films were treated for 3 min by the mixture of SC−CO_2 with HMDS (1%) or (for comparison) for 20 min by the mixtures of SC−CO_2 with ethanol (5%) or hexane (5%). The obtained films were dried at the temperature of about 100°C.

As a result, uniform dielectric hydrophobic films were produced. Characterization of their structure, mechanical properties, dielectric constants, is presented next.

EXPERIMENTAL RESULTS AND DISCUSSION

To investigate the structure of our CTAB/TSC-2/TEOS films treated by solutions of HMDS, ethanol, and hexane in SC−CO_2, we used transmission electron microscopy (TEM). These films exhibited the same structure as untreated CTAB/TSC-2/TEOS films, that is, our films probably contained randomly distributed micropores 1–2 nm in diameter (see [9,17]).

We measured hardness, H, and Young's modulus, E, of our films using the standard nanoindentation technique. Obtained data on H and E are summarized in Table 1.

The dielectric constant k of the films was measured at different temperatures by means of the capacitance method for the frequency of the applied voltage $f = 100$ kHz. Sample heating was realized using a special furnace table. Film thickness was evaluated by means of the profiler, or, together with the refractive indices, by the prism coupler.

TABLE 1 Some Physical Properties of the CTAB/TEOS/TSC-2 Films

Dielectric film	Film thickness (nm)	Minimal hardness (GPa)	Minimal Young's modulus (GPa)	Refractive index	Dielectric constant at 100 kHz
CTAB (25 mM)/butanol–water (22:5)/TEOS (1 M)/TCS-2 (50 mM)/HCl (0.1 M) film	800 (2 layers)	0.9	7.2	1.4366	6.6
Same film heated and kept at 150°C	800 (2 layers)				3.6
Same film heated and kept at 200°C	800 (2 layers)				3.4
CTAB (25 mM)/butanol–water (22:5)/TEOS (1 M)/ TCS-2 (50 mM)/HCl (0.1 M) film treated for 24 h in stirring HMDS and heated for 1 h at 420°C in the vacuum furnace	813 (2 layers)	1.3–1.8	8–13	1.4083	3.8
Same film heated and kept at 150°C	813 (2 layers)				3.2
Same film heated and kept at 200°C	813 (2 layers)				3.1
CTAB (25 mM)/butanol–water (22:5)/TEOS (1 M)/ TCS-2 (50 mM)/HCl (0.1 M) film treated for 3 min in SC–CO_2 + HMDS (1%)	790 (2 layers)	1.5–1.8	11–13		4.6
Same film heated and kept at 150°C	790 (2 layers)				3.8
CTAB (25 mM)/butanol–water (22:5)/TEOS (1 M)/ TCS-2 (50 mM)/HCl (0.1 M) film treated for 20 min in SC–CO_2 + ethanol (5%)	770 (2 layers)	~1	~8		6.9
Same film heated and kept at 150°C	770 (2 layers)				4.1
CTAB (25 mM)/butanol–water (22:5)/TEOS (1 M)/ TCS-2 (50 mM)/HCl (0.1 M) film treated for 20 min in SC–CO_2 + hexane (5%)	780 (2 layers)	1.0–1.2	8–10		7.2
Same film heated and kept at 150°C	780 (2 layers)				4.2

The obtained data on k measured at different temperatures are also represented in Table 1. It is evident that heating of the films leads to the absorbed moisture evaporation and, hence, to the decrease of k (see Table 1).

It is clear from Table 1 that anti-absorption treatment of dielectric films with HMDS considerably increases their mechanical properties and low dielectric constant (see [9]). Indeed, HMDS makes the film surfaces hydrophobic by reacting with Si–OH bonds to form stronger hydrophobic $Si-O-Si(CH_3)_3$ bonds.

Treatment of the films with the HMDS solution in $SC-CO_2$ also decreases k (approximately to the same values as for films treated with pure HMDS) and makes its values quite stable over time. It improves the mechanical properties of the films even more. It can be explained by easier penetration of this solution into the film pores.

However, treatment of the films with solutions of ethanol and hexane in $SC-CO_2$ was less effective (see Table 1). Indeed, such treatment only washed out humidity from the film pores but did not make the films hydrophobic.

CONCLUSION

We have fabricated the novel CTAB/TEOS/TSC-2-based Si-substrate-supported microporous films with strong mechanical properties and low value of dielectric constant. An optimal anti-absorption treatment of these films can be produced by treatment with HMDS and solution in $SC-CO_2$. These treatment procedures considerably improve the film's mechanical properties and decrease its dielectric constant, making it stable over time.

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