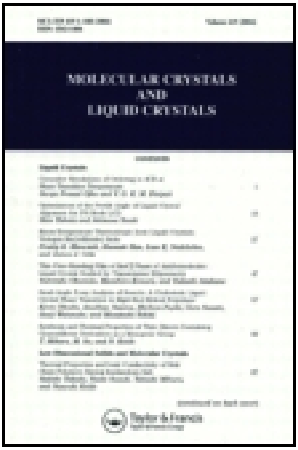

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Characterization of the CTAB/NaSal/TEOS Solid Films—Prospective Candidates for Application as Low-Dielectric-Constant Interlayers

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Version of record first published: 17 Oct 2011

To cite this article: Andrei A. Sonin, Jong-Baek Seon, Min-Ho Yang & Hyun-Dam Jeong (2006): Characterization of the CTAB/NaSal/TEOS Solid Films—Prospective Candidates for Application as Low-Dielectric-Constant Interlayers, Molecular Crystals and Liquid Crystals, 451:1, 33-40

To link to this article: http://dx.doi.org/10.1080/154214090960018

Mol. Cryst. Liq. Cryst., Vol. 451, pp. 33–40, 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214090960018

Characterization of the CTAB/NaSal/TEOS Solid Films—Prospective Candidates for Application as Low-Dielectric-Constant Interlayers

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We present a complex investigation of the structure and mechanical and dielectric properties of the CTAB/NaSal/TEOS films spin-coated on silicon wafers. These novel films can be used as the low-dielectric-constant interlayers in microelectronics. It is shown that the films have average disordered structure: they consist of a great number of several hundred nanometer-sized domains, which contain mutually parallel cylindrical tubes, having diameters of the order of 5 nm and length of several hundred nanometers. The mechanical characteristics of our films are found to be rather high with respect to those of other films for low-dielectric-constant applications. Minimal hardness and Young's modulus are 2.7 and 29.6 GPa respectively. The value of dielectric constant is around 3, and, in spite of chemical antimoisture absorption treatment, some small amount of water is present in the film.

Keywords: calcination; low-*k* materials; precursor solution; self-assembly; spin-coating; worm-like micelle

INTRODUCTION

Substances with low values of dielectric constant (denoted as k in the electronic materials reviews and thus called "low-k materials") have

Authors are grateful to Dr. V. S. Bezborodov for helpful discussions and to Dr. G. P. Semenkova for her assistance in preparation of precursor solutions. A. A. Sonin thanks SAIT for financial support during his stay in Korea.

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potential for application in the electronic industry [1]. The use of such substances as dielectric interlayers in electronic chips gives both considerable increase of the electric impulse propagation speed and reduction of dielectric losses.

The low-*k* materials should possess the following essential properties: possible lower values of dielectric constant and high mechanical modulus, in order to withstand severe conditions.

The first is often achieved by using dielectric materials containing pores (i.e., large fractions of air). The second is achieved by spatial (crystalline) ordering of pores.

One procedure, initially proposed for fabrication of the low-*k* materials with spatially ordered pores, is the so-called "liquid crystal templating" method [2,3]. When this technique is used, a lyotropic liquid crystalline phase, built by aggregates of surfactant molecules (micelles) or polymer chains, serves as a template for further formation of a solid low-*k* material. Initially, a mixture of a dielectric inorganic substance (e.g., some silicon-containing compound) with an organic lyotropic phase is prepared. In this mixture (often called a "precursor solution"), the inorganic material occupies the continuous solvent region and, in the course of reaction of hydrolysis [4], creates inorganic walls between the surfactant micelles or polymer chains. This is the so-called "self-assembly" [5] of surfactant (polymer) and inorganic material in the bulk of a solvent.

Thin solid films can be obtained by deposition of the precursor solution on solid substrates (on silicon wafers for electronic applications) by spin- or dip-coating.

Further on, the organic material is removed by calcination—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. 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.

A prospective dilute template for preparation of the dielectric films with spatially ordered pores is the equimolar water solution of cationic cetyltrimethylammonium bromide (CTAB) surfactant, $CH_3(CH_2)_{15}-(CH_3)_3N^+-Br^-$, and sodium salicylate (NaSal) salt, *ortho*-$OH-C_6H_4-COO^--Na^+$. This solution contains worm-like micelles several hundred nanometers in length and several nanometers in diameter [6–8] (Fig. 1).

The mechanism of formation of the worm-like micellar phase for this system is the following (see, e.g., [6]). Because of electrostatic interaction, the strongly binding Sal^- ions penetrate between $(CH_3)_3N^+$ CTAB surfactants heads, increasing the distance between them. This

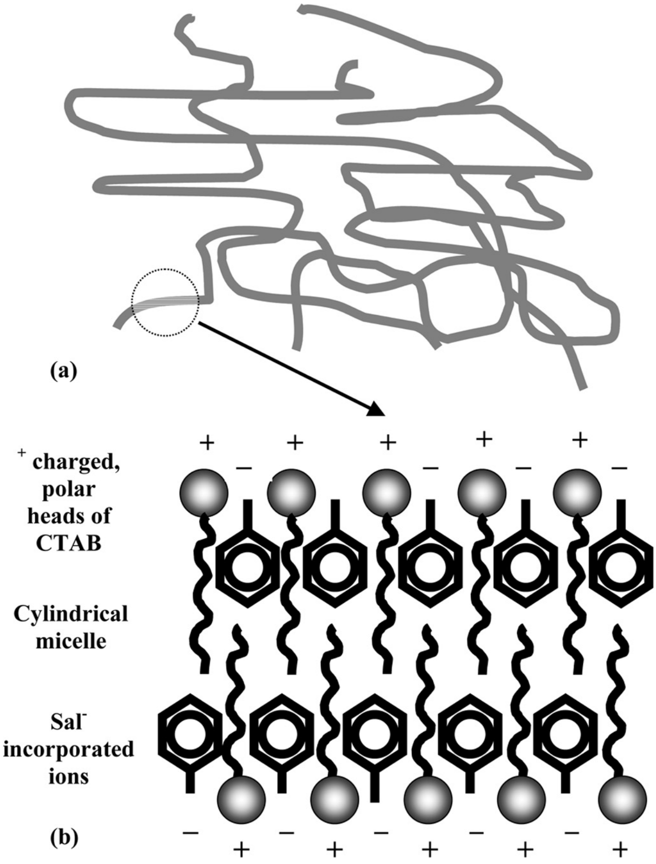

FIGURE 1 Schematic representation of the worm-like micelles (a) and their internal structure (b).

leads to creation of energetically favorable cylindrical (or worm-like, for larger scales) packing (Fig. 1).

In this work we make a detailed study of the structure and physical properties of the Si substrate–supported dielectric films, obtained on the basis of the previously described micellar template.

METHODOLOGY

In our experiments we used a dilute water-based precursor solutions of the following compositions:

1. CTAB: 5–50 mM/l;
2. NaSal: 5–50 mM/l;
3. 1 M/l of the silicon-containing material tetraethyl orthosilicate (TEOS), $Si(OC_2H_5)_4$; and
4. 0.1 M/l of the hydrochloric acid, HCl.

The precursor solution was obtained as follows. First, the CTAB/NaSal/water worm-like micelle–containing mixture was prepared. The CTAB/NaSal molar ratio for this solution, as was mentioned, was fixed to 1:1 (in most cases, 25 to 25 mM). CTAB was dissolved in deionized (Millipore) water by active stirring and heating of the mixture up to 60°C for 1 h. NaSal was then added, and the mixture was again stirred at room temperature for 1 h and left to equilibrate for a minimum of 3 days to obtain a homogeneous gel. Further on, TEOS was added, and the resulting emulsion was actively stirred at room temperature for a minimum of 1 h. And, finally, to accelerate the hydrolysis reaction, HCl was added, and the mixture was actively stirred until it became transparent.

The resulting precursor solution was then spin-coated with a speed of 3000 rpm on pure Si wafers or on Si wafers covered with Ti + Al electrode. Further on, the obtained substrate-supported films were soft- and hard-baked for 1 min at 150°C and 250°C respectively. Finally, the films were calcinated for several hours at 450°C.

EXPERIMENTS AND RESULTS

Film Structure

To study the structure of the obtained Si wafer–supported solid dielectric films, we used transmittion electron microscopy (TEM).

Figure 2 represents typical TEM images of the monolayer (approximately 200–250 nm thick) CTAB/NaSal/TEOS film spin-coated on a pure Si wafer. These images clearly show the presence of the several

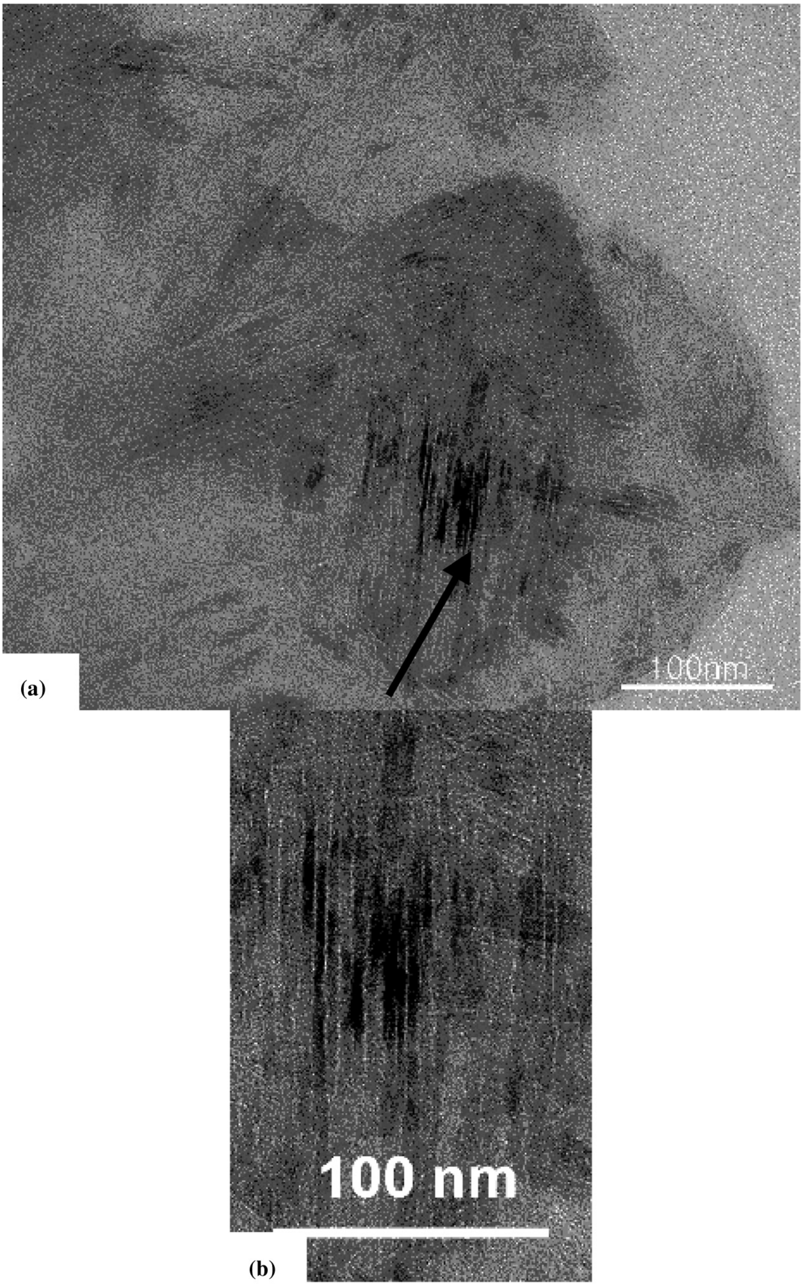

FIGURE 2 TEM images of the CTAB (25 mM)/NaSal (25 mM)/TEOS monolayer film, spin-coated on a pure Si wafer: (a) general view, showing an array of domains with ordered structure; (b) view of a single domain indicated by an arrow in (a).

hundred nanometer domains, containing mutually parallel cylindrical pores several hundred nanometers in length and 5 nm in diameter. It is evident that these pores are formed in the silicon-containing matrix by the worm-like micelles (micellar template), which have been burned out in the process of calcination. Indeed, geometrical sizes of pores correspond to sizes of worm-like micelles.

Because the film consists of domains with ordered internal structure, one should expect that it should demonstrate quite high values of mechanical parameters.

Mechanical Properties

To measure hardness and Young's modulus of the obtained films, we used the nanoindentation technique. The mechanical forces acting on the indentor (the atomic force microscope cantilever) were measured in dependence on its penetration depth into the film.

The results for three-layer CTAB/NaSal/TEOS film spin-coated on pure Si wafer are shown in Fig. 3. The minimal hardness and Young's modulus of this film are found to be 2.7 GPa and 29.6 GPa, respectively. These are, indeed, very high values! For comparison, for SiLK low-*k* material, these parameters are 0.38 GPa and 2.45 GPa respectively (i.e., one order of magnitude lower [9]).

Dielectric Properties

Dielectric constant, *k*, of our films was estimated from the capacitance measurements. For this the CTAB/NaSal/TEOS three-layer film was sandwiched between the lower, supporting, Si wafer with Ti + Al

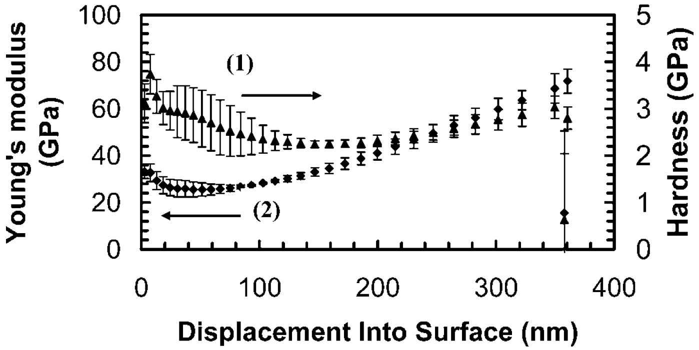

FIGURE 3 Results of nanoindentation measurements of the CTAB (25 mM)/NaSal (25 mM)/TEOS three-layer film: hardness (curve 1); Young's modulus (curve 2).

electrode and the upper, multiple, circular-shape, 1-mm diameter Ti + Al electrodes. Both types of electrodes were fabricated by means of the electron beam vacuum evaporation.

The film capacitance, *c*, was determined using a standard capacitance measurement table. An ac electric voltage of different frequencies was applied in series between three circular-shape upper electrodes and the lower electrode. Then the obtained *c* mean value was used to calculate the dielectric constant. For comparative analysis we used results on *k* obtained at $f = 100\,\text{kHz}$.

Initially founded values of *k* were quite high—of the order of ten. This was due to the absorption of the atmospheric humidity by dielectric films.

To decrease the absorption, the Si wafer + (Ti + Al) electrode–supported dielectric films were kept for 24 h in a stirring silylating agent hexamethyldisilizane (HMDS), $(CH_3)_3{-}Si{-}NH{-}Si{-}(CH_3)_3$. HMDS was also directly spin-coated on the film surface. HMDS made the film surfaces hydrophobic, reacting with Si–OH bonds and forming $Si{-}O{-}Si(CH_3)_3$.

Further on, the films were heated in a vacuum furnace at 420°C to eliminate resting water, absorbed by the film bulk.

As a result, the minimal obtained value of *k* was around 3, which indicated that in spite of these precautions, some insignificant humidity absorption by the films still was present.

CONCLUSION

In summary, we have made a study of the structure and mechanical and dielectric properties of the CTAB/NaSal/TEOS films spin-coated on silicon wafers. We showed that these films consist of domains several hundred nanometers in size, which contain mutually parallel cylindrical tubes, with diameters of the order of 5 nm and lengths of the order of several hundred nanometers. Minimal hardness and Young's modulus of the films were found to be 2.7 and 29.6 Gpa, respectively. These are quite high values with respect to those of other dielectric films for low-*k* applications. The films' dielectric constant value was around 3. This indicated that in spite of antimoisture absorption treatment by HMDS, some small amount of absorbed water rested in the films. Our results show that the investigated dielectric films have potential for applications as low-*k* interlayers.

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