Molecular Crystals and Liquid Crystals

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

Electric Field-Induced Ordering of the Worm-Like Micelles: Application to the Low-Dielectric-Constant Materials

Andrei A. Sonin [a], Mu-Gyeom Kim [a], Kwang-Hee Lee [a], Joo-Young Kim [a], Hyun-Dam Jeong [a] & Mahn-Won Kim [b c d]

[a] Electronic Materials Laboratory, Samsung Advanced Institute of Technology, Suwon, Korea

[b] Advanced Materials Engineering Department, Korea

[c] Advanced Institute of Science and Technology, Taejon, Korea

[d] Department of Materials, University of California, Santa Barbara, USA

Version of record first published: 31 Aug 2006

To cite this article: Andrei A. Sonin, Mu-Gyeom Kim, Kwang-Hee Lee, Joo-Young Kim, Hyun-Dam Jeong & Mahn-Won Kim (2006): Electric Field-Induced Ordering of the Worm-Like Micelles: Application to the Low-Dielectric-Constant Materials, Molecular Crystals and Liquid Crystals, 452:1, 27-36

To link to this article: http://dx.doi.org/10.1080/15421400500377644

Mol. Cryst. Liq. Cryst., Vol. 452, pp. 27–36, 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500377644

Electric Field–Induced Ordering of the Worm-Like Micelles: Application to the Low-Dielectric-Constant Materials

Andrei A. Sonin
Mu-Gyeom Kim
Kwang-Hee Lee
Joo-Young Kim
Hyun-Dam Jeong
Electronic Materials Laboratory, Samsung Advanced Institute of Technology, Suwon, Korea

Mahn-Won Kim
Advanced Materials Engineering Department, Korea Advanced Institute of Science and Technology, Taejon, Korea and Department of Materials, University of California, Santa Barbara, USA

We propose a new method to form solid, silicon-containing, substrate-supported films with ordered cylindrical pores. Such films may be used as low-dielectric-constant interlayers in microelectronics. First, liquid films are obtained in a plane-parallel glass capillary, using a precursor solution of the worm-like micelles as a template. An ac electric field of the order of 10^4 V/cm is applied to orient the micelles in one direction. Further on, after solidification of the precursor solution under the field and its calcination in a vacuum furnace, solid dielectric films are formed. These films possess high mechanical modulus and are expected to have low dielectric constants.

Keywords: calcination; Fredericks transition; liquid crystal templating method; low-*k* materials; precursor solution; worm-like micelles

INTRODUCTION

Substances with low dielectric constants, k (the so-called low-k materials), are widely used in electronic industry (e.g., [1]). As dielectric

Address correspondence to A. A. Sonin, Department of Physics, Moscow State Technical University "MAMI," 38, B. Semenovskaya, Str., Moscow 107023, Russia. E-mail: sonin_andrei@mail.ru

interlayers in electronic chips, they strongly increase the speed of propagation of electric impulses and reduce dielectric losses.

In most cases, low-k materials are silicon-containing substances with spatially ordered pores. The presence of pores makes k lower, whereas the pores' ordering increases mechanical properties of the material. Such substances are commonly produced by the so-called "liquid crystal templating" method (e.g., [2–4]), when some liquid crystalline (precursor) solution is used as a template for further fabrication of the silicon-based solid substance (or film). Solid material (film) is obtained in the course of the hydrolysis reaction. Pores result from the calcination (keeping the substance in a vacuum furnace at several hundred degrees °C) to burn out the organic liquid crystalline template.

One of the effective ways of increasing the pore ordering in a low-k material (and, hence, of improving its mechanical properties) is the aligning of molecular aggregates in a precursor template solution by some external force "flow, field." The elongated-form worm-like micelles, or polymer chains of the liquid crystalline template, will orient themselves along the direction of this force (see Fig. 1). Indeed, both the worm-like micelles and polymers have been already unidirectionally aligned by a hydrodynamic flow (e.g., [5–7]), micelles by a magnetic field (e.g., [8,9]) and polymers by a dc electric field (e.g., [10,11]).

Spatial ordering induced by the action of an external force can be then preserved in a solidified state and further on after calcination. Porous materials obtained by this method are expected to have a considerable pore bulk fraction (i.e., low k values) and strong mechanical properties.

In this article we propose and experimentally test a new, original method of the ac electric field–induced orientation of the worm-like micelles in a precursor solution. We also describe and test the

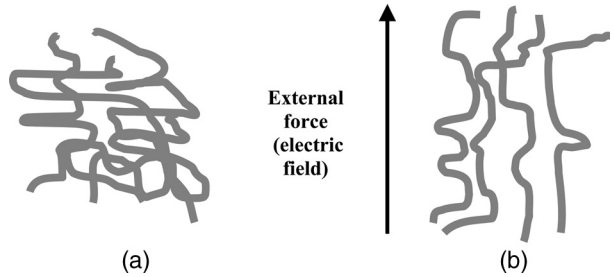

FIGURE 1 Schematic representation of the worm-like micelle-containing system: (a) disordered micelles and (b) micelles ordered by an external force.

procedure of preparation of solid porous dielectric films using the proposed technique.

The advantage of our method, with respect to the previously used force-induced ordering procedures, is its simplicity. Indeed, all earlier techniques used for ordering of the worm-like micelles and polymer chains in precursor solutions are quite complex. The alignment of micelles by a hydrodynamic flow and by a magnetic field is hardly realizable in industrial conditions. The former method demands a special Couette cell, whereas the latter one requires a massive electromagnet, giving a sufficient field of the order of 10 T. The orientation of the worm-like micelles or polymer chains by a dc electric field may often be complicated by an electric charge transport.

METHODOLOGY

In our experiments we used a water-based precursor solution of the following composition:

1. 5–50 mM/l of the cationic cetyltrimethylammonium bromide (CTAB) surfactant, $CH_3(CH_2)_{15}-(CH_3)_3N^+-Br^-$;
2. 5–50 mM/l of the strongly binding sodium salicylate (NaSal) salt, *ortho*-$OH-C_6H_4-COO^--Na^+$;
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.

Details on preparation of precursor solutions are reported by us in [4].

Both the worm-like micelle containing CTAB/NaSal/water solution (solution 1) and CTAB/NaSal/TEOS/HCl/water precursor solution (solution 2) were utilized for measurements.

The optimal condition for formation of the worm-like micelles in our system is the equimolar ratio of CTAB and NaSal. In this case, the strongly binding Sal^- ions easily penetrate between $(CH_3)_3N^+$ CTAB surfactants heads and increase the distance between the latter. As a result, energetically favorable cylindrical (or worm-like, for larger scales) packing is being formed. For more details on this issue see, for example, Refs. [4] and [12].

For optical measurements, both solutions 1 and 2 were placed into standard liquid crystal (LC) cells consisting of two plane-parallel glass substrates with transparent indium tin oxide (ITO) electrodes (Fig. 2a). For preparation of solid films, one of the glass substrates was replaced by a rectangular peace of Si wafer, covered with Ti + Al electrode-layer (Fig. 2b). The lower substrate of the LC cell was separated from the

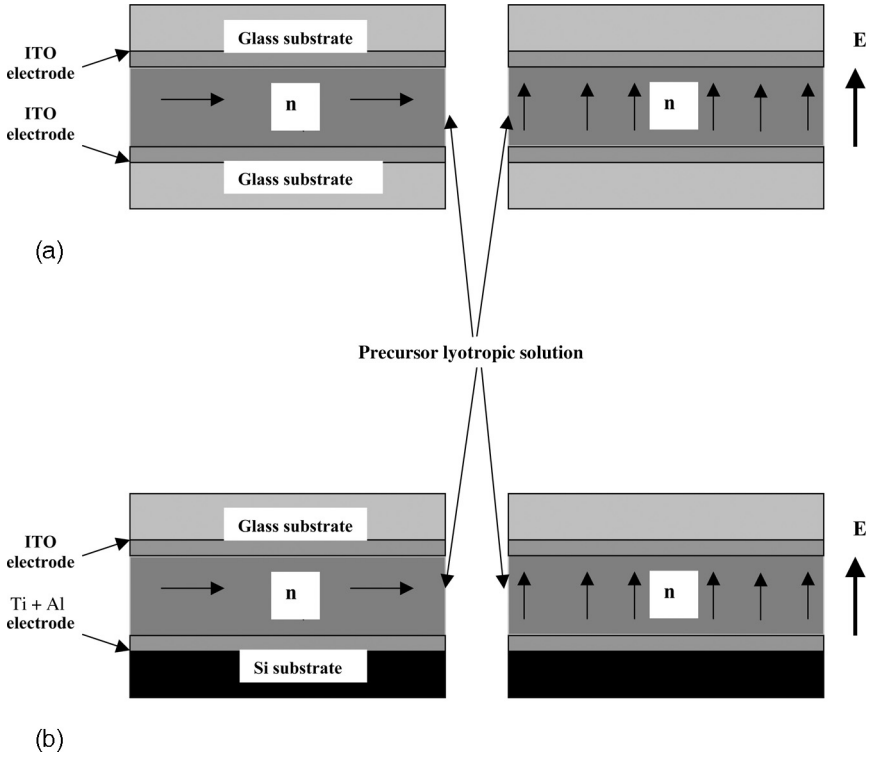

FIGURE 2 Experimental cells used for polarization-optical studies (a) and for preparation of solid dielectric films (b). Director, **n**, shows the mean orientation of the micelle long axes.

upper one by the 3.5-μm-diameter polystyrene ball spacers. The thickness of an empty cell was measured by means of the light interference method and was found to lie within the 3.7–4.5-μm interval.

EXPERIMENTS AND RESULTS

The prepared samples (LC cells containing solutions 1 and 2) were studied by means of the standard polarization-optical technique (see, e.g., [13]). The polarization-optical setup included an He-Ne laser, polarizer, cell-holder, analyzer, photomultiplier, lock-in amplifier, and synchronic detector.

We measured the intensity of light, I, transmitted by a sample, placed between crossed polarizer and analyzer, dependent on the applied ac sinusoidal voltage. The voltage was supplied by the

functional generator within the 0–16-V interval. Unfortunately, higher voltages were not attainable because of frequent dielectric breakdowns of the samples.

The worm-like micelles' long axes were oriented parallel to the substrates of the LC cells (planar alignment) by a hydrodynamic flow in a process of the cell filling (see Fig. 2). The cells were placed between the crossed polarizer and analyzer at a 45° angle by its orientation axes to obtain the maximal transmitted light intensity.

As has already been mentioned, the mechanism of orientation of the worm-like micelles or polymer chains in a dc electric field may be quite complex because of the migration of electric charges. However, in a quite high-frequency ac electric field the charge transport is negligible, and the orientation process takes place because of the interaction between the applied electric field and the dielectric anisotropy of the medium. This is the so-called Fredericks transition (e.g., [14]). This effect bears a threshold character—the reorientation starts from a certain value of applied electric voltage: $U_F = \pi[(4\pi K)/\Delta\varepsilon]^{1/2}$. Here K is average elastic module of the precursor solution; $\Delta\varepsilon$ is its dielectric anisotropy.

Complete micelle (polymer) reorientation (parallel or perpendicular to the applied electric field, depending on the sign of dielectric anisotropy) takes place at the so-called saturation electric voltage, $U_{sat} \gg U_F$.

In the studied case of the worm-like micelles, we can speak about the reorientation of the director **n** (a unit vector showing the mean orientation of the long micelle axes); see Fig. 2.

Mechanical properties of dielectric films should certainly depend on the conditions of the film preparation, in particular, on the applied ac electric field frequency. Indeed, hardness and Young's modulus of the film have the higher values; the higher is the degree of the pore spatial ordering. The latter is induced by the applied electric field and should depend on the field frequency. For low electric field frequencies ($f \ll f_{opt}$, optimal experimental frequency), the electric charge transport is important. It can damage the pore ordering and hence decrease mechanical modulus of the film. For higher frequencies (of the order of f_{opt}), the charge transport is negligible, and the degree of the pore ordering and mechanical modulus of the film should be higher.

Figure 3 shows time dependencies of I measured for different frequencies of the applied voltage ($U = 16\,V$) for solution 1. Using data represented in Fig. 3, we have chosen the optimal frequency for our experiments: $f_{opt} = 1\,kHz$. Such value of frequency is most often utilized for electro-optical measurements of liquid crystals. Note that not only the charge transport but also the contribution from the Kerr effect at this frequency is negligibly small in our system (e.g., [15]).

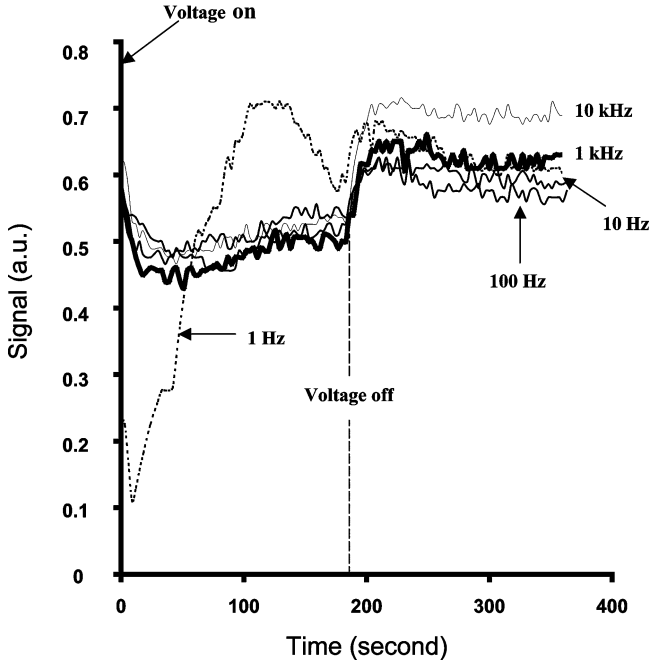

FIGURE 3 Time dependencies of the transmitted light intensity measured for different frequencies of the applied voltage ($U = 16\,\text{V}$) for solution 1 (composition: CTAB, 25 mM/l; NaSal, 25 mM/l). The cell thickness $h = 4.1\,\mu\text{m}$.

Figure 4 shows time dependencies of the transmitted light intensity, I, for different applied voltages for solution 1. The inset to this figure represents the same for solution 2.

The difference in the values of I of this figure and of the inset is most probably related to different initial degree of the micelle orientation. In the former case it is higher than in the latter one.

The Fredericks effect threshold voltage for both solutions is about 2 V. When the voltage is further increased, the transmission intensity is decreased. This means that the worm-like micelles (or director **n**) tend to orient themselves parallel to the electric field (positive dielectric anisotropy), that is, perpendicular to the cell walls (Fig. 2).

It is evident from Fig. 4 that the voltage response and relaxation times for both solutions are quite long—of the order of 100 s. This can be explained by specific structure and viscous properties of the studied worm-like micelle–containing systems (e.g., [16,17]).

Finally, we tried to fabricate the electric field–ordered solid films on the basis of our precursor solution (solution 2). With this purpose we

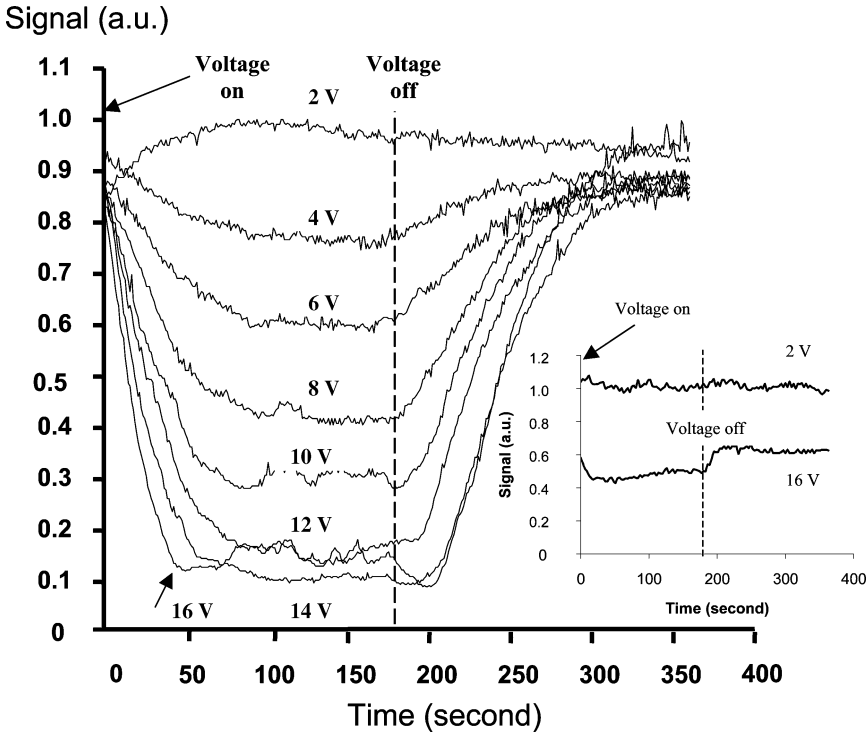

FIGURE 4 Time dependencies of the transmitted light intensity measured for different values of the applied ac voltage ($f = 1\,\text{kHz}$) for solution 1 (composition: CTAB, 25 mM/l; NaSal, 25 mM/l). The cell thickness $h = 3.7\,\mu\text{m}$. In the inset: the same for solution 2 (composition: CTAB, 25 mM/l; NaSal, 25 mM/l; TEOS, 1 M/l; HCl, 0.1 M/l). The cell thickness $h = 4.1\,\mu\text{m}$.

filled several LC cells, having one Si + (Ti + Al) substrate (see Fig. 2b), with the precursor solution 2. Further on, the 1-kHz-frequency 16-V electric voltage was applied, and the samples were kept in it for several hours at 60°C. As a result, the precursor solution was solidified. By taking off the upper glass substrates, we obtained solid dielectric films on Si + (Ti + Al) wafers. These films were further kept for 1 min, respectively, at 150 and 250°C (soft and hard baking) and for several hours at 450°C in a vacuum furnace (calcination) to evaporate resting water and to burn out the organic substances.

Unfortunately, considerable thickness (several μm) and inhomogeneous free surface of the obtained electric field–ordered solid films at present make their structural investigations (TEM) and measurements of their dielectric constant difficult. Note, however, that we expect

TABLE 1 Mechanical Properties of Some Dielectric Films

Dielectric film	CTAB/NaSal/TEOS			SiLK [18]
	Without electric field	In Electric field	Spin-coated film [4]	
Hardness, GPa	2.5	3.0	2.7	0.38
Young's modulus, GPa	28.5	30.5	29.6	2.45

that our films should have ordered structure and low values of k. Indeed, this may be concluded from our study of the films prepared from precursor solution 2 by spin-coating on Si wafers and by further baking and calcination [4]. Our TEM analysis of these films shows the presence of domains containing mutually parallel cylindrical pores several μm in length and 50 nm in diameter. Our capacitance measurements give $k < 3$ for these films (there is some water absorption).

Nevertheless, we have managed to characterize the mechanical properties of our films. By means of a nanoindentation method, we have measured the minimal values of hardness and Young's modulus for two solid films prepared according to the previously described procedure, without application of the external electric field and in the field, respectively (see Table 1). The second film shows higher values of the mechanical parameters than the first one. In our opinion, this is due to the electric field–induced micelle (and, consequently, pore) ordering.

Note that the minimal values of hardness and Young's modulus for the analogous films spin-coated on Si wafers (without application of the electric field) [4] are of the same order of magnitude. For comparison, for commonly used SiLK low-k material (e.g., [18]), the latter mechanical parameters are one order of magnitude lower (see Table 1).

By means of the atomic force microscopy, we have also estimated the mean surface roughness, R, of the previously mentioned two films (prepared without and with application of electric field). The same tendency of improvement of the film quality due to the action of an external field is observed: for the film prepared without application of the field, $R = 0.65$ nm, whereas the surface of the electric field–ordered film is smoother, $R = 0.55$ nm.

CONCLUSION

In summary, we have proposed and experimentally studied a novel simple method of the ac electric field unidirectional alignment of worm-like micelles in a precursor solution. Solid dielectric Si

wafer-supported films were produced by means of the proposed technique, and their mechanical properties and surface roughness were measured. It was found that the micelle electric field–ordering increased the mechanical properties and decreased the surface roughness of the obtained solid films. These films are also expected to have low dielectric constants and, hence, could be used as low-k interlayers in microelectronics.

Nevertheless, it is clear that further work on the improvement of the quality of the obtained dielectric films (i.e., on making their surface smoother and their thickness lower and homogeneous) is needed.

ACKNOWLEDGMENTS

A. A. Sonin thanks Samsung Advanced Institute of Technology (SAIT) for financial support during his stay in Korea.

REFERENCES

[1] Maex, K., Baklanov, M. R., Shamiryan, D., Iacopi, F., Brongersma, S. H., & Yanovitskaya, Z. S. (2003). Low dielectric constant materials for microelectronics. *J. Appl. Phys.*, *93*, 8793.

[2] Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., & Beck, J. S. (1992). Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Lett. Nature*, *359*, 710.

[3] Fan, H., Reed, S., Baer, T., Schunk, R., Lopez, G. P., & Brinker, C. J. (2001). Hierarchically structured functional porous silica and composite produced by evaporation-induced self-assembly. *Microporous and Mesoporous Mater.*, *44–45*, 625.

[4] Sonin, A. A., Seon, J.-B., Yang, M.-H., & Jeong, H.-D. (2006). Characterization of the CTAB/NaSal/TEOS solid films – prospective candidates for application as low-dielectric-constant interlayers. *Molec. Cryst. Liquid Cryst.*, *451*, 33.

[5] Kim, W.-J. & Yang, S.-M. (2000). Flow-induced silica structure during in situ gelation of wormy micellar solutions. *Langmuir*, *16*, 4761.

[6] Kim, W.-J. & Yang, S.-M. (2001). Helical mesostructured tubules from taylor vortex-assisted surfactant templates. *Adv. Mater.*, *13*, 1191.

[7] Chen, Z.-R., Kornfield, J. A., Smith, S. D., Grothaus, J. T., & Satkowski, M. M. (1997). Pathways to macroscale order in nanostructured block copolymers. *Science*, *277*, 1248.

[8] Tolbert, S. H., Firouzi, A., Stucky, G. D., & Chmelka, B. F. (1997). Magnetic field alignment of ordered silicate-surfactant composites and mesoporous silica. *Science*, *278*, 264.

[9] Firouzi, A., Schaefer, D. J., Tolbert, S. H., Stucky, G. D., & Chmelka, B. F. (1997). Magnetic-field-induced orientational ordering of alkaline lyotropic silicate-surfactant liquid crystals. *J. Amer. Chem. Soc.*, *119*, 9466.

[10] Thurn-Albrecht, T., DeRouchey, J., Russell, T. P., & Jaeger, H. M. (2000). Overcoming interfacial interactions with electric fields. *Macromolecules*, *33*, 3250.

[11] Thurn-Albrecht, T., Schotter, J., Kästle, G. A., Emley, N., Shibauchi, T., Krusin-Elbaum, L., Guarini, K., Black, C. T., Tuominen, M. T., & Rusell, T. P. (2000).

Ultrahigh-density nanowire arrays grown in self-assembled diblock copolymer templates. *Science*, *290*, 2126.

[12] Olsson, U., Söderman, O., & Guéring, P. (1986). Characterization of micellar aggregates in viscoelastic surfactant solutions. A nuclear magnetic resonance and light scattering study. *J. Phys. Chem.*, *90*, 5223.

[13] Blinov, L. M. & Chigrinov, V. G. (1994). *Electrooptic Effects in Liquid Crystal Materials*, Springer-Verlag: New York.

[14] De Gennes, P. G. & Prost, J. (1993). *The Physics of Liquid Crystals*, 2nd ed., Oxford University Press: Oxford, U.K.

[15] Oizumi, J., Kimura, Y., Ito, K., & Hayakawa, R. (1996). Electric birefringence relaxation spectroscopy of linear micelles in aqueous cetyltrimethylammonium bromide solutions with sodium salicylate. *J. Chem. Phys.*, *104*, 9137.

[16] Kim, W.-J. & Yang, S.-M. (2000). Microstructures and rheological responses of aqueous CTAB solutions in the presence of benzyl additives. *Langmuir*, *16*, 6084.

[17] Kuramada, K.-I., Itakura, S., Nagamine, S., & Tanigaki, M. (1997). Effect of the transient network structure on the growth of microparticles through aggregation. *Langmuir*, *13*, 3700.

[18] Martin, S. J., Gadschalx, J. P., Mills, M. E., Shaffer, II E. O., & Townsend, P. H. (2000). Development of a low-dielectric-constant polymer for the fabrication of integrated circuit interconnect. *Adv. Mater.*, *12*, 1769.