Hexagonal to Lamellar Mesostructural Changes in Silicate Films Caused by Organic Additives

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The presence of dopant molecules and cosolvents in the sols from which mesostructured silicate thin films are pulled can have profound influences on the resulting structure and long range order. Dopants are frequently desired in order to induce a function such as luminescence. An important luminescent molecule, carbazole, is very effective at converting the film mesophase from hexagonal to lamellar. A very small change in the mole ratio of carbazole to the structure-directing surfactant, from 0.41 to 0.44, causes a very abrupt change of the structure of CTAB-templated mesostructured silica from two-dimensional hexagonal to lamellar. A molecule with a very similar structure, fluorene, also affects the structure in a similar manner, but much higher concentrations are necessary and the final order is not as high. Molecules having similar functional groups (especially amine groups) but nonplanar structures show that both the shape and the presence of the amine group play a role in causing the structural change. Many luminescent molecules require cosolvents in order to incorporate them into the sol from which the films are pulled. The effects of cosolvents, especially THF and benzene, on the structures of the films are also studied. The reasons for the structural change from 2-d hexagonal to lamellar as the concentrations of these molecules are increased are discussed in terms of modifications in the effective shapes of the micelles, and subtle local effects on the hydrolysis and condensation reaction rates caused by the basic aromatic amine functional group.

Introduction

Incorporation of photoactive molecules in mesostructured silicate films is attracting increasing interest.[1−4] In the one-step, one-pot synthesis approach, all components, including the photoactive molecules and the structure-directing agents, are dissolved in the starting sol. The dip coating of this sol onto a substrate produces doped mesostructured films. The earliest one-step, one-pot preparations of films used luminescent molecules that were designed to probe the film formation.[5−7] In these studies, very low concentrations of a luminescent probe were used to monitor micelle formation and to correlate this process with changes in solvent composi-

tion during the rapid film formation. Probes that are preferentially incorporated in, and report the properties of, specific regions of the film are therefore used, and the final films contain the luminescent molecules in the specific locations. Recently, deliberate placement of luminescent molecules in three spatially separated regions of mesostructured films (the silicate matrix, the hydrophobic core of surfactant micelles, and the intervening ionic interface between surfactant headgroups and the silica framework) was reported.[8] Designed placement of two or more molecules simultaneously has also been demonstrated.[9]

The formation of structured films with long range order is a delicate process that can be easily disrupted. The long range order is especially sensitive to the presence of dopant molecules. Frequently a desired molecule is insoluble in the starting sol and cosolvents are needed. The choice of cosolvents is limited because they can easily prevent the formation of high quality films or inhibit the formation of long range order. Even the relative humidity and the concentration of alcohol vapor in the film-pulling environment can drastically affect the structure. In addition, the film quality is

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Table 1. Structural Changes Caused by Organic Dopants and Co-solvents

additive	additive wt (g)	additive/CTAB mole ratio	vol. THF (mL)	d-spacing (H) (Å)	d-spacing (L) (Å)	mesophase
carbazole	0.05	0.12:1	17	29.6		hexagonal
	0.08	0.19:1	17	30.3		hexagonal
	0.17	0.41:1	17	35.3		hexagonal
	0.18	0.44:1	17		34.0	lamellar
	0.2	0.50:1	17		30.5	lamellar
	0.5	1.23:1	17		32.6	lamellar
	0.3	0.62:1	20 (benzene)		29.7	lamellar
diphenylamine	0.075	0.18:1	17	34.4		hexagonal
	0.15	0.36:1	17	32.2	30.7	mixed
	0.3	0.76:1	17	32.0	30.7	mixed
	0.5	1.2:1	17		30.6	lamellar
fluorene	0.2	0.53:1	17	34.5		hexagonal
	0.3	0.79:1	17		34.2	lamellar
	0.4	1.06:1	4		37.3	lamellar
diphenylmethane	0.4	1.6:1	5	33.9		hexagonal
	0.5	1.2:1	17	32.7	26.5	mixed
	0.8	1.6:1	17	34.4	26.2	mixed
triphenylamine	0.3	1:1	4	35.6		hexagonal
	0.75	2.25:1	7.5	38.6		hexagonal
	0.4	0.71:1	17	32.8	25.7	mixed
	0.7	1.31:1	17	34.8	25.8	mixed
triphenylmethane	0.3	1.16:1	2	35.6		hexagonal
	0.3	0.5:1	17	32.4	25.0	mixed
	0.5	0.8:1	17	33.5	25.5	mixed
	0.8	1.3:1	17	36.0	25.4	mixed

sensitive to the composition of the initial sol; the acidity and concentrations of reactants severely constrain the range of preparations that can be used successfully.

During the course of our studies of CTAB-templated hexagonal phase silica films doped with carbazole, we discovered that carbazole is very effective at converting the film mesophase from hexagonal to lamellar. A very small change in the amount of carbazole causes a very abrupt change of the structure. CTAB-templated meso-structured silica evolves from hexagonal through cubic to lamellar structures upon increasing the concentration of CTAB in the starting sol.[5] At the concentration of CTAB added to the sol in our study (3.5 wt %), only the hexagonal mesostructure is formed. In the dip-coating process, a substrate is slowly withdrawn from the sol reservoir. The moving substrate entrains the sol, forming an initially liquid film. The film thins by solvent and gravitational draining and its profile is wedge-shaped until it reaches a thickness (~150−200 nm) beyond which it is essentially constant.[10−12] Concurrent with this process is the formation of both silica and micelles and their transformation into the ordered mesostructure. The presence of dopants can profoundly influence the nature of the final structure.

In this paper we report the results of our studies of the effects of dopant molecules and of cosolvents on the structures of surfactant-templated thin films. Carbazole (Scheme 1), a widely used dopant in sol−gel silicates,[13] has the greatest effect on the structure; a change in the mole ratio of carbazole to surfactant from 0.41 to 0.44 causes the structure to change from 2-d hexagonal to lamellar. The latter structure is very highly ordered. A molecule with a very similar structure, fluorene (Scheme

Scheme 1

Carbazole   Fluorene   Diphenylamine
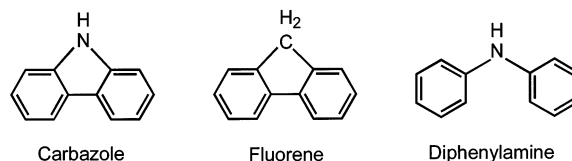
1), also affects the structure in a similar manner, but much higher concentrations are necessary and the final order is not as high. Both of these molecules have planar structures; experiments with molecules having similar functional groups (especially amine groups) but non-planar structures show that both the shape and the presence of the amine group play a role in causing the structural change. Many molecules require cosolvents in order to incorporate them into the sol from which the films are pulled. The effects of cosolvents, especially THF and benzene, on the structures of the films are also studied. The reasons for the structural change from 2-d hexagonal to lamellar as the concentrations of these molecules are increased are discussed in terms of changes in the shape and size of the hydrophobic region of the micelle relative to that of the ionic headgroup.

Experimental Section

Sol Preparation. The sol was prepared by refluxing 61 mL of TEOS (Aldrich), 61 mL of ethanol, 4.8 mL of water, and 0.2 mL of 0.07N HCl (mole ratio 1:3.8:1:5 × 10⁻⁴) at 60 °C for 90 min. Then 0.1 mL of deionized water, 0.4 mL of 0.07 N HCl, and 7.7 mL of ethanol were added to 3.3 mL of the sol and stirred for 10 min to prepare the stock solution. This procedure is designed to hydrolyze TEOS but minimize the siloxane condensation rate.[14] The films are prepared using the stock solution with dopant molecules and cosolvents as described below. Table 1 lists the dopant molecules that were studied and the resulting film mesostructures.

Carbazole Sol. To prepare the sol containing carbazole, 17 mL of THF was added to 11.5 mL of the stock solution. The

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Table 2. Structural Changes Caused by THF

vol. THF (mL)	vol. EtOH (mL)	THF/CTAB mole ratio	d-spacing (H) (Å)	d-spacing (L) (Å)	mesophase	wt % THF
5	19.7	25:1	33.6		hexagonal	18%
7.7	17	41:1	31.3	25.4	mixed	28%
17	7.7	84:1	32.2	26.0	mixed	60%
21.7	3	109:1	35.6	25.2	mixed	75%

concentration of HCl in the sol is 2.7 mM with this amount of THF. To the sol was then added 0.05−0.5 g (0.01−0.10 M) of carbazole and finally 3.5 wt % CTAB (0.82−0.91 g, or 0.081−0.088 M, depending on the amount of carbazole used). The final molar proportions of the constituents were 1 TEOS:22.5 EtOH:5 H_2O:0.011 HCl:29.6 THF:0.32−0.35 CTAB:0.042−0.42 carbazole. In one preparation, 20 mL of benzene was added to a sol with 0.3 g carbazole to examine the effect of benzene as a cosolvent.

Fluorene Sol. To prepare the sol containing fluorene, 17 mL of THF was added to 11.5 mL of the stock solution. To the sol was then added 0.1−0.5 g fluorene (0.02−0.11 M) and 3.5 wt % CTAB (0.83−0.84 g, or 0.082−0.083 M). The final molar proportions of the constituents were 1 TEOS:22.5 EtOH:5 H_2O:0.011 HCl:29.6 THF:0.32−0.33 CTAB:0.085−0.42 fluorene. In one preparation only 4 mL of THF was added to a sol with 0.4 g fluorene.

Diphenylamine Sol. For the preparation of diphenylamine sol, again 17 mL of THF was added to 11.5 mL of the stock solution. Diphenylamine (0.075−0.5 g, 0.02 − 0.10 M) and 3.5 wt % CTAB (0.82−0.84 g, or 0.081−0.083 M) were then added to the sol. The final molar proportions of the constituents were 1 TEOS:22.5 EtOH:5 H_2O:0.011 HCl:29.6 THF:0.32−0.33 CTAB:0.063−0.42 diphenylamine.

Diphenylmethane Sol. For the preparation of diphenyl-methane sol, 17 mL of THF was added to 11.5 mL of the stock solution. To the sol were then added 0.5−0.8 g diphenyl-methane (0.10−0.17 M) and 3.5 wt % CTAB (0.90−1.08 g, or 0.087−0.104 M). The final molar proportions of the constitu-ents were 1 TEOS:22.5 EtOH:5 H_2O:0.011 HCl:29.6 THF:0.35−0.42 CTAB:0.42−0.67 diphenylmethane. In addition, in some sol preparations 0.2−0.4 g of diphenylmethane and 3.5 wt % CTAB (0.51−0.57 g, or 0.085−0.095 M) in 5 mL of THF were made to examine the effect of a smaller amount of THF on the film mesophase. In these cases, the final molar proportions of the constituents were 1 TEOS:22.5 EtOH:5 H_2O:0.011 HCl:8.7 THF:0.15−0.18 CTAB:0.17−0.34 diphenyl-methane.

Triphenylamine Sol. To prepare the sol containing triphenyl-amine, 17 mL of THF was added to 11.5 mL of the stock solution. 0.4 or 0.7 g of triphenylamine (0.057 or 0.100 M, respectively), and 3.5 wt % CTAB (0.84 or 0.80 g, or 0.081 or 0.076 M, respectively) were then added. The final molar proportions of the constituents were 1 TEOS:22.5 EtOH:5 H_2O:0.011 HCl:29.6 THF:0.31−0.33 CTAB:0.23−0.40 triphenyl-amine. In two sol preparations, 4 and 7.5 mL of THF were used with 0.3 and 0.75 g, respectively, of triphenylamine.

Triphenylmethane Sol. For the preparation of triphenyl-methane sol, 17 mL of THF was added to 11.5 mL of the stock solution. Triphenylmethane (0.3−0.8 g; 0.043−0.115 M) and 3.5 wt % CTAB (0.91−0.93 g, or 0.088−0.134 M) were then added. The final molar proportions of the constituents were 1 TEOS:22.5 EtOH:5 H_2O:0.011 HCl:29.6 THF:0.35−0.36 CTAB:0.17−0.46 triphenylmethane. In one sol preparation 2 mL of THF was used in a sol with 0.3 g triphenylmethane.

Sol Preparation with Cosolvents Only. *Tetrahydrofuran Sol.* To examine the sole effect of THF on the mesostructure formation in the sol−gel films, a few sols containing only the THF cosolvent were made. Several molar ratios of THF:EtOH (0.3:1−5.2:1) were used. Table 2 lists the amounts of THF and EtOH that were used and the resulting film mesostructures.

Benzene Sol. For films containing benzene but without any organic dopant molecules, the sol composition had to be modified to obtain high quality films. A 5-mL aliquot of the starting sol, 0.2 mL of deionized water, and 0.6 mL of 0.07 N HCl were mixed and stirred for 15 min, followed by a dilution

Table 3. Structural Changes Caused by Benzene

benzene/CTAB mole ration	d-spacing (Å)	d-spacing calcined (Å)	mesophase	wt % benzene
0:1	37.8		hexagonal	0%
4:1	34.8	28.0	hexagonal	3%
10:1	35.6	31.8	hexagonal	7%
20:1	35.1	30.1	hexagonal	13%
30:1	31.8	no peaks	lamellar	18%

with 2 equiv of ethanol. CTAB (3.5 wt %) was then added to the sol, and benzene was added last. In most experiments a benzene/CTAB mole ratio of 30:1 or less was used; details are listed in Table 3.

Film Pulling. The films were withdrawn using the equip-ment described previously.[10] Polished Si (100) substrates (9 cm × 1 cm × 0.5 mm) or typical microscope slides cut in half (7.5 cm × 1.25 cm × 1 mm) were cleaned in a hot bath of 4 parts H_2SO_4 and 1 part H_2O_2 for half an hour. The substrates were then rinsed with deionized water and transferred to a deionized water bath that was then heated to boiling for 30 min. Finally, the substrates were rinsed and stored in deion-ized water prior to use. These substrates were withdrawn at a speed of 5 cm/min from the sols described above. A cover was placed on top of the sol reservoir to reduce air currents and to slow the evaporation rate. Convection-free drying produces high-optical-quality films.

Characterization of the Films. *XRD and TEM.* The film mesostructures were characterized by X-ray diffraction (XRD) patterns using a locally constructed X-ray diffractometer. Ni-filtered Cu Kα radiation at $\lambda = 1.5418$ Å was used. The ranges of XRD measurements were usually from 1.5 to 50° 2θ. In some experiments, calcination of the films at 400 °C for 4 h was carried out to remove the surfactant. XRD patterns taken before and after calcination often assist in the determination of the mesostructure present in the films.

Transmission electron microscopy (TEM) was used to image films containing carbazole or diphenylamine. The films were scraped off the substrate surface and dispersed in ethanol, and then drops of the ethanol solution were added to Cu grids. TEM images were taken using a JEOL model 100 CX electron microscope operating at 100 keV.

Luminescence Spectroscopy. Luminescence spectra of car-bazole and diphenylamine in the mesostructured and pure silica films, in THF, EtOH, and water, and in powder form, were taken using a Spex Fluorolog spectrofluorometer. The films were excited at 290 nm.

Results

Structural Changes Caused by Dopant Mol-ecules. The effects of dopant molecules on the structure of the mesostructured thin films are presented in this section. Carbazole (Scheme 1) has the most striking effect: a small change in the concentration causes a sharp change in the film structure from 2-d hexagonal to lamellar. Other dopant molecules have similar effects, but larger concentration changes are necessary to cause the structure to change from 2-d hexagonal to lamellar. Figure 1 illustrates the change of micellar mesophase from 2-d hexagonal to lamellar during film formation upon the incorporation of carbazole dopant molecules.

Structural Changes Caused by Carbazole. Figures 2 a−c show the XRD patterns of 3.5 wt % CTAB sol−gel
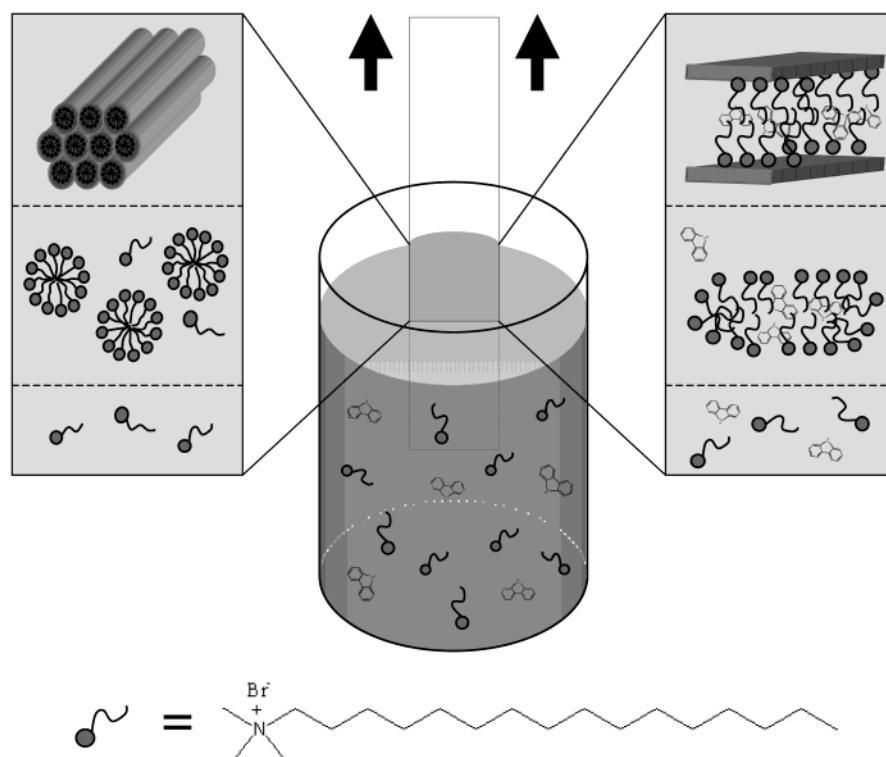
Figure 1. Schematic diagram of the film pulling process. The panel on the left shows (from bottom to top) the changes that occur as the individual surfactant molecules form micelles and finally form an ordered 2-dimensional hexagonal structure. The panel on the right shows the same sequence when carbazole is present. Incorporation of carbazole in the evolving micelle promotes the formation of the lamellar phase structure.

silica films with various amounts of carbazole added to the sol. Table 1 lists the sol conditions and the corresponding surfactant mesophases exhibited in the films. The amount of THF cosolvent in the sol is the same in all cases.

At a carbazole/CTAB mole ratio at or below 0.41:1, the XRD patterns suggest that the mesostructure present in the films is 2-d hexagonal with the typical (100) and (200) peaks, as shown in Figure 2a. (The XRD peaks are indexed according to the literature assignments for the different phases of mesostructured films[5] and are described in terms of those structures for clarity in describing the films.) The transition to the lamellar phase structure starts to occur with the addition of slightly more carbazole to the sol, as shown in Figure 2b with a carbazole/CTAB mole ratio of 0.44:1. The film mesostructure is mixed, but still is primarily hexagonal at this carbazole concentration. At a still higher carbazole/CTAB mole ratio (0.5:1), the film mesostructure becomes completely lamellar, similar to that shown in Figure 2c. Figure 2c shows the XRD pattern of a film with a carbazole/CTAB mole ratio of 1.23:1. Similar XRD patterns have been reported in the lamellar mesostructured sol−gel films templated with surfactant sodium dodecyl sulfate (SDS).[6,7]

The *d*-spacing for the lamellar phase (001) peak is 32.6 Å, and the average spacing between adjacent peaks is 2.75° 2θ. These values are significantly different from those of the films without addition of carbazole. A peak marked with an asterisk is due to a carbazole aggregate; this peak also appears in the carbazole powder XRD pattern as the most intense peak. The crystallite size is estimated to be about 500 Å using the Sherrer equation.[15]

The structural changes induced by carbazole are not unique to the films prepared from sols using THF as the cosolvent. For example, benzene is another cosolvent that mixes well with the sol and produces excellent quality films. In the absence of carbazole, the structure is 2-d hexagonal, but when carbazole is added to the sol containing benzene, the XRD patterns reveal that the films possess pure lamellar mesostructure. The XRD pattern of a 3.5 wt % CTAB sol−gel film with a carbazole/CTAB mole ratio of 0.62:1 and benzene/CTAB mole ratio of 82:1 shows the *d*-spacing for the (001) peak of the lamellar phase is 29.7 Å, and the average spacing between adjacent peaks is also 2.75° 2θ. The concentration data are listed in Table 1.

Structural Changes Caused by Fluorene. Fluorene has a structure similar to that of carbazole but with the −NH group replaced by a −CH$_2$ group. It is interesting to determine if fluorene can also be used to modify the film mesostructure. Table 1 lists some selected fluorene sol conditions and the resulting film mesostructures. XRD patterns of the CTAB sol−gel films at different fluorene/CTAB mole ratios before and after calcination were taken to determine the film mesostructures. At a fluorene/CTAB mole ratio of 0.53:1, the film mesostructure is hexagonal, as shown in Figure 3 a. Calcination of the film at 400 °C for 4 h leads to a slight shrinkage in *d*-spacing from 34.5 to 28.5 Å (or 17%) for the (100) peak, but the film still maintains the well-organized hexagonal phase structure. When the fluorene/CTAB mole ratio is increased to 0.79:1, the film mesostructure is lamellar, as shown in Figure 3b, and the diffraction

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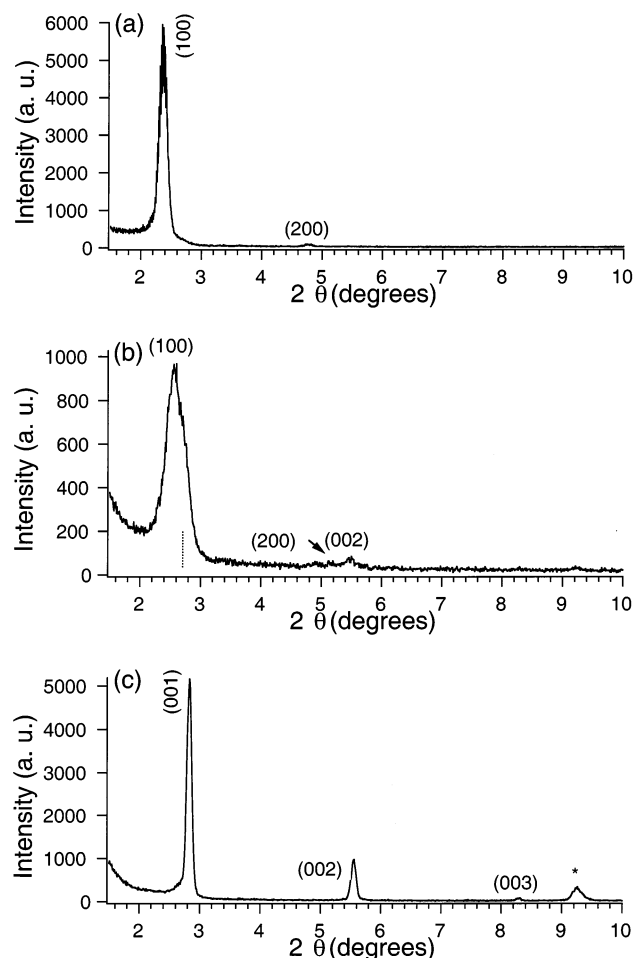
Figure 2. X-ray diffraction patterns as a function of increasing carbazole concentration. (a) XRD pattern of a 3.5 wt % CTAB sol−gel silica film with a carbazole/CTAB mole ratio of 0.2:1. (b) XRD pattern at a carbazole/CTAB mole ratio of 0.44:1. The dashed line at 2.70° 2θ indicates the expected location of the (001) peak, and the asterisk indicates the peak from the ordered packing of carbazole. (c) XRD pattern at a carbazole/CTAB mole of 1.23:1.

peaks disappear after calcinations because removal of surfactant leads to the collapse of the layered structure. Higher-order peaks (i.e., diffraction peaks beyond the second-order peak) never appear in the fluorene-containing films even when the film mesostructure is lamellar. It is interesting to note that the intensity of the second-order peak in the lamellar phase films is usually much stronger than that of the second-order peak of the hexagonal phase films.

Structural Changes Caused by Diphenylamine. Diphenylamine has a structure related to that of carbazole, but the absence of the C−C bond between the phenyl rings allows the molecule to become nonplanar. Table 1 lists the sol conditions and the mesophases formed in the films containing diphenylamine. At low concentrations of diphenylamine in the sol, the film mesophase is hexagonal as expected. When the amount of diphenylamine is raised to a diphenylamine/CTAB mole ratio of 0.36:1 the XRD pattern suggests the presence of a mixed phase structure in the films. Diffraction peaks from hexagonal and lamellar phases are associated with the (100) and (001) series of peaks, respectively. This result shows that at a mole ratio of 0.36:1 of diphenylamine/CTAB the phase transition from hexagonal to lamellar
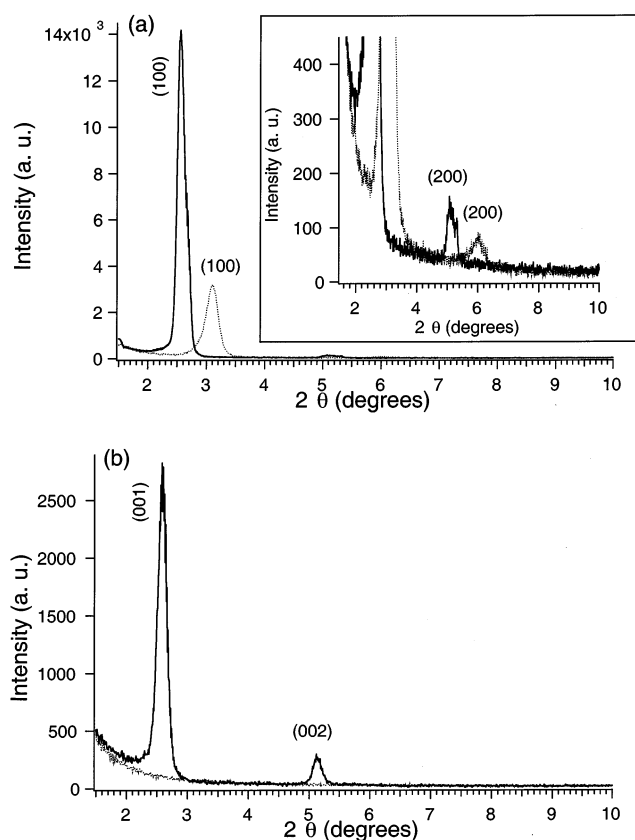

Figure 3. Effect of calcination on films containing fluorene. (a) XRD pattern of a 3.5 wt % CTAB sol−gel silica film with a fluorene/CTAB mole ratio of 0.53:1 before (solid line) and after calcination (dotted line). The peaks shift to higher 2θ angles after calcination. (b) XRD pattern at a fluorene/CTAB mole ratio of 0.79:1 before (solid line) and after calcination (dotted line). The diffraction peaks disappear after calcination.

begins to occur. The *d*-spacing for the (001) peak is 30.7 Å, and average spacing between adjacent peaks is 2.89° 2θ. A peak at 2.41° 2θ, and small peaks between 3 and 5° 2θ may be due to the presence of an *Ia3d* cubic phase. Such cubic phase structure has been reported in mesostructured silica powder templated with CTAB surfactant and diethyl ether as a cosolvent.[16] In that case the peak at 2.41° 2θ can be indexed as the (211) diffraction peak of the cubic phase structure, and the (220) peak is embedded under the (100) and (001) peaks (data not shown). TEM images and selected area electron diffraction patterns reveal the presence of cubic phase silica.

Films exhibit this mixed phase structure over a wide diphenylamine concentration. In fact, the mixed phase is still observed at a diphenylamine/CTAB mole ratio of 0.76:1, although at this concentration ratio the peaks arising from lamellar phase structure have stronger intensities.

A complete lamellar phase structure is observed when the diphenylamine/CTAB mole ratio reaches 1.2:1. The *d*-spacing for the (001) peak is 30.6 Å, and the average spacing between adjacent peaks is 2.89° 2θ.

Effect of Diphenylmethane, Triphenylamine, and Triphenylmethane. Three other organic additives of similar molecular structures have also been examined in this

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study. Diphenylmethane contains two phenyl rings as do carbazole and fluorene, whereas triphenylamine and triphenylmethane have three phenyl groups and a nonplanar triangular pyramidal-shaped structure. Table 1 lists the results of incorporating these molecules in the sols and the resulting mesophases formed in the films. The effects on the structures caused by using these organic additives are very similar: the films all have a mixed hexagonal and lamellar phase structure. When the amount of THF in the sol is relatively low, the films all maintain good hexagonal phase structure even when a very large amount of the organic dopant is added. Initially it was not clear whether the formation of the lamellar phase structure was caused by the organic additive or by the THF cosolvent. However, a close comparison of the XRD patterns of these mixed phase films and those of the pure THF films to be discussed later shows that the XRD patterns are all almost identical. The *d*-spacing for the (001) peak and average peak to peak spacing of about 3.45° 2θ are almost identical to those films prepared with only the cosolvent. The only noticeable difference is the clear presence of the (200) peak from the hexagonal phase structure. Therefore, it can be safely assumed that the lamellar phase structure arises primarily from the addition of THF and that the organic dopant molecules do not have a major structure-modifying effect.

Structural Changes Caused by Cosolvents. *Tetrahydrofuran.* A typical CTAB-templated sol−gel silica film possesses a 2-d hexagonal structure when prepared from the 3.5 wt % CTAB sols under the slightly acidic sol composition (pH = 5) that is used in this study. The XRD pattern of a typical 3.5 wt % CTAB film shows a *d*-spacing of 39.8 Å calculated from the strong and sharp first-order peak. To interpret the discovery that the addition of carbazole to the sol with THF as the cosolvent effectively transforms the film mesostructure from hexagonal to highly ordered lamellar, control experiments using organic cosolvents were carried out.

The effects of varying the concentrations of the THF cosolvent on the structure are listed in Table 2. A representative XRD pattern from a film made with a THF/CTAB mole ratio of 84:1, or 60 wt % of THF to the final sol, shows the film possesses a mixed-phase structure as X-ray diffraction peaks arising from both hexagonal and lamellar phase structures are present. The peak at 2θ = 2.77°, or *d*-spacing of 32.2 Å, corresponds to the (100) peak of the hexagonal mesophase structure. The (200) peak is not present in this sample, but it does appear in films prepared with a THF/CTAB mole ratio of 109:1 (or wt % THF = 75%). The lamellar phase structure is identified by the presence of several diffraction peaks with an average 2θ spacing of 3.44° that can be indexed as (001), (002), ... The *d*-spacing for the (001) peak at 2θ = 3.43° is 25.8 Å. The XRD patterns of films with other THF/CTAB mole ratios look very similar.

Benzene. Benzene is another cosolvent that can be used to incorporate organic dopant molecules in the sol because it mixes well with the sol and allows high quality films to be formed. Other possible cosolvents, such as chloroform and toluene, form gel particles while the sol is being stirred and are not suitable for the preparation of high quality films. Addition of benzene
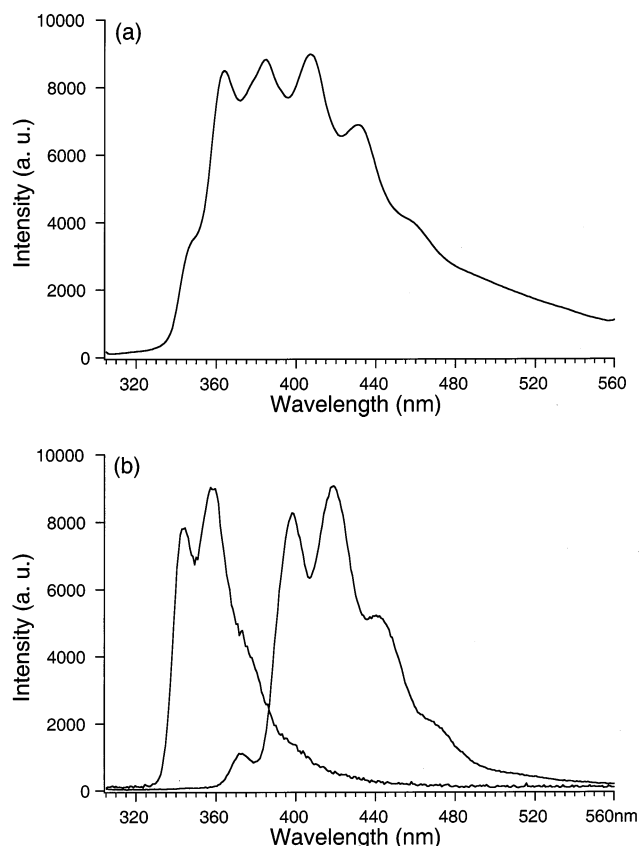

Figure 4. Luminescence spectra of carbazole. (a) Luminescence spectrum of a lamellar mesostructured thin film with a carbazole/CTAB mole ratio of 1.23:1. (b) Luminescence spectra of a THF solution of carbazole (peaks at 344 and 358 nm) and a pure silica film containing carbazole (peaks at 372, 398, 419, 440, and 468 nm).

to the sol gives films with well-ordered 2-d hexagonal mesostructure up to a benzene/CTAB mole ratio of 25: 1, as evidenced by the strong and sharp (100) and (200) peaks. XRD patterns of 3.5 wt % CTAB sol−gel silica films with different benzene/CTAB mole ratios before and after calcination at 400 °C for 4 h were taken to determine the film mesostructures. At a benzene/CTAB mole ratio of 20:1, retention of the X-ray diffraction peaks after calcination and the shift of the peaks to higher 2θ values is indicative of a slight shrinkage (∼14%) of the hexagonal mesostructure. At a benzene/ CTAB mole ratio of 30:1, the first-order diffraction peak is as strong as that from the 20:1 films, but the XRD shows loss of all the diffraction peaks after calcination suggesting that lamellar mesostructure is present at this mole ratio. At benzene/CTAB mole ratios higher than 50:1, the long-range order of the mesostructure gradually degrades, and the first-order diffraction peak loses much of its intensity and sharpness. Table 3 lists some selected sol conditions and the corresponding mesostructures present in the films.

Luminescence Spectra of Dopants. Luminescence spectra of carbazole in mesostructured sol−gel films, selected solvents, and in powder form were taken to investigate its location and distribution. Figure 4a shows the luminescence spectrum of a mesostructured sol−gel film with a carbazole/CTAB mole ratio of 1.2:1. At this mole ratio the film mesostructure is lamellar. In the luminescence spectrum, bands can be clearly identified at 350, 364, 385, 408, 431, and 460 nm. For

comparison, luminescence spectra of carbazole in a pure silica film (amorphous), in powder form, and in solution (THF, ethanol, H_2O, hexane, and heptane) were also taken. Selected spectra are shown in Figure 4b.

There is a blue shift in the luminescence spectra of carbazole in nonpolar solvents such as hexane and heptane compared to those of carbazole in polar solvents such as ethanol and THF. However, carbazole luminescence is not very sensitive to solvent polarity: the luminescence spectra in ethanol, THF, and water are almost identical (two major peaks at 344 and 358 nm). The luminescence spectrum of carbazole in the pure silica film (no CTAB added) was taken to see if some peaks present in the film luminescence could be attributed to carbazole residing in the silicate framework. A well-resolved spectrum was obtained with major peaks at 372, 398, 419, 440, and 470 nm. To determine if some carbazole luminescence may arise from aggregates, a powder emission spectrum was taken. The spectrum appears very similar to that of carbazole in the untemplated silica film except for a decrease in the intensity of the 398 nm peak. The results suggest that the film luminescence can be mainly attributed to carbazole associated with organic species, possibly the hydrocarbon tail of CTAB surfactant inside the micellar layers, and the silicate species of the silica framework layers. Further analysis of the results is presented in the following section.

Discussion

Incorporating dopant molecules into mesostructured sol−gel thin films in order to develop desired properties is an active area of research. The dopants are typically metal-containing molecules for applications to catalysis[17,18] and luminescencent molecules for optical studies such as laser action and energy transfer.[19,20] Frequently, the desired molecule is insoluble in the sol that is used to form the film, and a cosolvent is required. The choice of cosolvents is limited; the cosolvent must not only dissolve the desired dopant molecule but it also must be miscible with the starting sol (alcohol, water, and tetraalkoxy silane) without causing silane gelation and without deleteriously affecting either the film quality or the long range order. Two favorable solvents that are finding increasing use are THF and benzene; unfavorable solvents include dichloromethane, toluene, and diethyl ether. Many organic molecules (including those discussed in this paper) are insoluble in the moderately polar sol but are very soluble in nonpolar benzene or slightly polar THF.

Mesostructured silicate thin films that are templated by CTAB exhibit structures that are dependent on the concentration of the structure-directing agent in the sol. Structures that have been reported to date include hexagonal (2.5 wt % CTAB), cubic (4.2 wt % CTAB), and lamellar (5.0 wt % CTAB) mesostructures at different

wt % of CTAB in the sol.[5,21] The sol compositions were very similar to that used in this study. Figure 5 illustrates the hexagonal and lamellar film mesostructures and their corresponding XRD patterns. Films containing organic dopants and associated cosolvents that are used as probes of the film formation process or to produce desired optical properties exhibited the same mesostructure (with slightly different cell constants) as the undoped counterparts.

Sensitivity of Structure to Carbazole. Surprisingly, a relatively small change in the amount of carbazole, a luminescent organic molecule, causes a dramatic phase change. Before the carbazole addition, a mixed-phase structure is present in the films due to the presence of THF. When carbazole is added to the 3.5 wt % CTAB-containing sol at a carbazole/CTAB mole ratio of 0.1:1, the mesophase is completely hexagonal. There is also a sharp phase transition from hexagonal to lamellar. At a carbazole/CTAB mole ratio of 0.41:1, the film mesophase is still hexagonal. However, when the ratio is slightly increased to 0.44:1, a partial lamellar phase is present, and at 0.5:1 the film mesophase is transformed completely to lamellar.

The film mesophase change from hexagonal to lamellar is accompanied by a change in the lattice spacing of the mesostructure as carbazole concentration is increased. The *d*-spacing of the (100) peak for the hexagonal phase structure increases from 29.6 to 35.3 Å as the carbazole/CTAB mole ratio increases from 0.1:1 to 0.41:1. The transformation of the mesophase to lamellar decreases the lattice spacing. The (001) peak *d*-spacing for the lamellar phase structure falls to 29.5−32.5 Å. There is a reversal in the trend of lattice spacing, with the mixed phase having the largest lattice spacing.

Sensitivity of Structure to Other Related Molecules. The complete transformation of film mesostructure from hexagonal to lamellar is much more gradual for the diphenylamine−THF sol. At very low concentrations of diphenylamine in the sol, the resulting film mesostructure is hexagonal. There is a wide range of the intermediate mixed phases present in the films over the diphenylamine/CTAB mole ratios of 0.36:1−0.76:1. At a mole ratio of 1.2:1, a complete highly ordered lamellar-phase film is formed. Therefore carbazole is a more effective structure-modifying agent than diphenylamine.

Location of Carbazole by Luminescence Spectroscopy. Fluorescence emission spectra of carbazole in the mesostructured films, amorphous silica films, powder, and in various solvents provide additional information on the location and distribution of carbazole in the mesostructured films. As shown in Figure 4b, the luminescence spectrum of carbazole in THF contains two major peaks at 344 and 358 nm and the spectrum of carbazole in a pure silica film (no CTAB added) consists of a well resolved, red-shifted progression with major peaks at 372, 398, 419, 440, and 470 nm. The spectrum of the lamellar mesostructured thin film (Figure 4a) contains emission intensity in both regions. The results suggest that carbazole molecules are associated with the organic species that can be in the proximity of THF molecules or the hydrocarbon tail of

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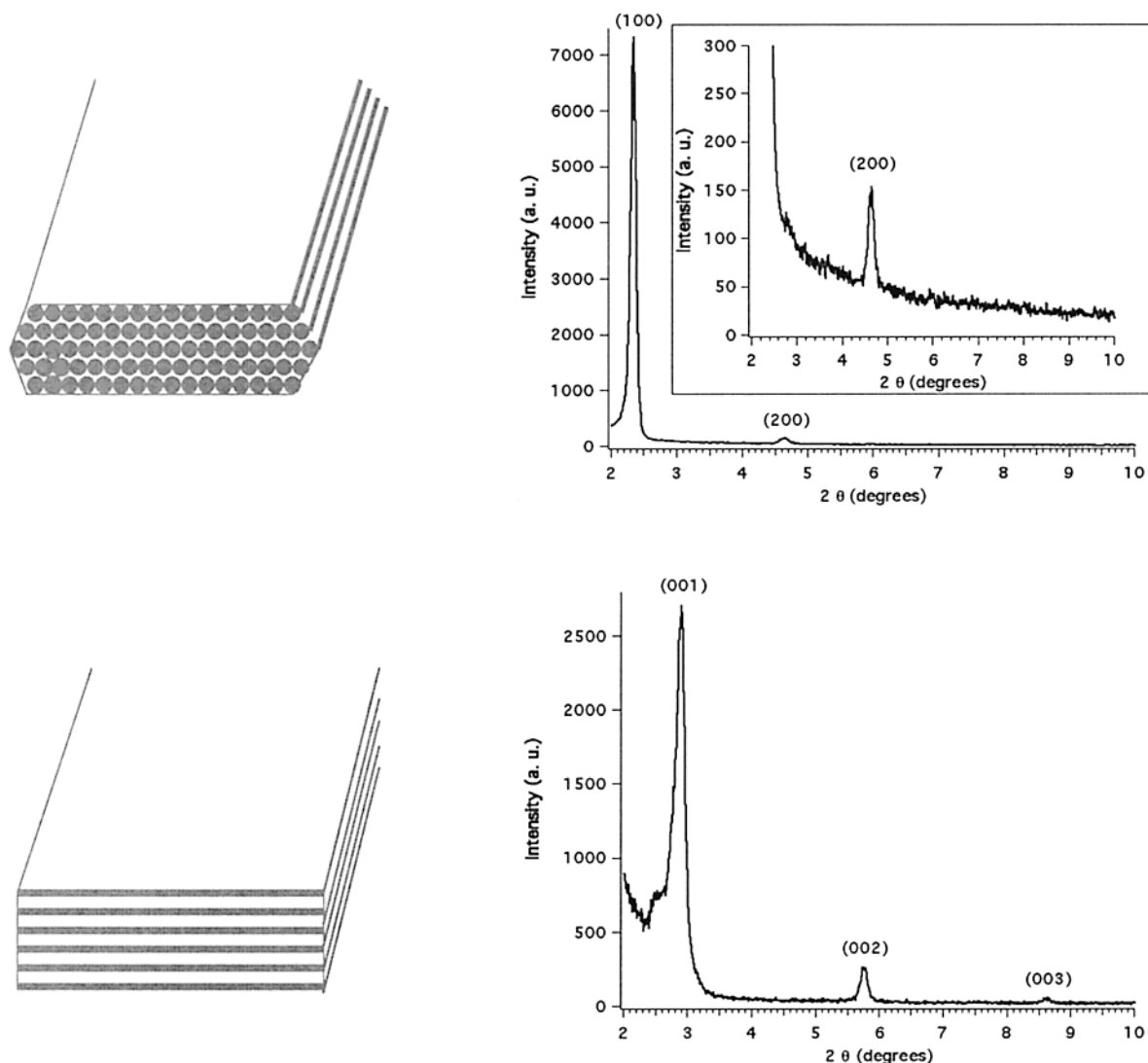(21) Raman, N.; Anderson, M. T.; Brinker, C. J. *Chem. Mater.* **1996**, *8*, 1682.

Figure 5. Sketches of the structures of 2-d hexagonal and lamellar mesophases and their corresponding XRD patterns. The XRD pattern shown for the hexagonal phase structure (top) is obtained from a film pulled from a 3.5 wt % CTAB sol without any organic additive. The XRD pattern shown for the lamellar phase structure is obtained from a film with a diphenylamine/CTAB mole ratio of 1.2:1.

the CTAB surfactant, and that some fraction of carbazole is in the silicate-rich environment of the inorganic framework. The fact that locations of carbazole fluorescence peaks in THF, ethanol, and water are similar limits a more detailed quantitative analysis of the site distribution. It is probably not possible for all of the carbazole to be incorporated in the micellar interior when the carbazole/CTAB mole ratio is 1.2:1, and some of the carbazole may reside in the inorganic silicate region.

Explanation of the Phase Change and the Co-Solvent Effect. The phase changes caused by addition of dopant molecules is related to geometric changes governing micelle formation. The ratio of the size between the polar headgroup and that of the hydrophobic tail determines the solubility of the surfactant molecules in aqueous solution and its aggregation behavior. The surfactant packing parameter[22] provides an empirical criterion for predicting the shape that the aggregates of a given surfactant will adopt. The packing

parameter P is given by $P = v/LA_0$ where v is the volume occupied by the hydrophobic moiety of the amphiphilic molecule, L is the critical length in the fully extended conformation, and A_0 is the surface area occupied by a hydrophilic headgroup at the water−aggregate interface. Both L and v can be calculated for a saturated hydrocarbon chain of n carbon atoms using Tanford's equations:[23] $L = (1.5 + 1.265n)$ Å and $v = (27.4 + 26.9n)$ Å^3. Specific values of P are associated with spherical micelles ($P < 1/3$), wormlike micelles ($1/3 < P < 1/2$), vesicles ($1/2 < P < 1$), flat bilayers ($P = 1$), and inverted micelles ($P > 1$).[24]

Surfactant phase transformation from hexagonal to lamellar is a result of the reduction of micellar curvature from cylindrical to a more elongated planar structure induced by the incorporation of organic cosolvent molecules into the hydrophobic interior of micelle. For example, adding varying amounts of an organic solute (e. g., benzene or hexanol) to the sol during the prepara-

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tion of silicate−CTAB liquid crystals at high pH (pH = 12.5) changes the structure.[25] Silicate−CTAB liquid crystals with hexagonal morphology were formed by using little or no organic solute (benzene/CTAB molar ratio of 2.3:1 or less). At higher benzene concentration (benzene/CTAB molar ratio of 3.5:1) or by addition of straight chain alcohols such as hexanol (hexanol/CTAB molar ratio of 1.3:1), lamellar phases were produced. This result was attributed to the swelling of the hydrophobic regions of the aggregates, leading to reduced curvature of the hydrophobic−hydrophilic aggregate interfaces.[26,27] In terms of the values of P during the phase transformation, P should increase from $^1/_3 < P < ^1/_2$ to a value close to 1.

In this study of mesostructured thin film formation there are two organic additives in the sol: a luminescent molecule that is added as dopant and an organic cosolvent. The effect of cosolvent was examined as a control experiment. The explanation given above for the cause of phase transformation from hexagonal to lamellar by the incorporation of dopant molecules into the hydrophobic interior of the micellar structures formed during the film formation process can be reasonably applied to incorporation of solvent molecules. However, the amount of benzene or THF that is needed to cause such an effect is much higher for our slightly acidic initial sol. For example, THF is one of the few cosolvents that can change the mesophase of silica powders from ordered hexagonal phase to lamellar phase when the weight percent of cosolvent to the micellar solution is 20−30%.[16] However, in our film study with THF, a complete transformation from the hexagonal mesophase to lamellar mesophase is not observed, even when the weight percent is 60−75%. On the basis of the relative X-ray diffraction peak intensities from both phases, there is still a large portion of the hexagonal phase structure. These results suggest the amount of THF incorporation into the micellar structure is not high enough or the cosolvent effect is not strong enough under the sol condition used for film preparation. Similar results are obtained with benzene as the cosolvent. Even though the phase transformation from 2-d hexagonal to lamellar does occur, lamellar phase structure is not observed in the XRD patterns of benzene-containing sol−gel films until a benzene/CTAB mole ratio of 30:1 is used.

Effect of the Amine Functional Group. Part of the reason that carbazole and diphenylamine can have such a dramatic effect in directing the film mesophase from a highly ordered hexagonal structure to a highly ordered lamellar structure can be attributed to their substantial incorporation into the micellar interior during the film formation process. But such a simple view is not adequate to explain the fact that other organic additives of similar structures (i.e., diphenylmethane, triphenylamine, and triphenylmethane) do not cause such an effect. The shape of the dopant molecule may play a role. A planar molecule like carbazole may efficiently diffuse into the micellar interior, and affect the packing arrangement of the surfactant molecules to adapt a

lamellar structure. A bulkier molecule such as triphenylamine with a triangular pyramidal molecular structure may not be incorporated efficiently into the hydrophobic interior because its large incorporation may disrupt the packing order of surfactant and weaken the micellar structure. Thus, it is ineffective in causing mesophase modification.

In addition, the −NH group on carbazole and diphenylamine are important, as diphenylmethane does not have a structure modification effect, and fluorene, even though it does produce lamellar phase at high concentrations, does not give as extensive long range order and thus higher-order diffraction peaks as does carbazole. Carbazole and diphenylamine are aromatic amines and are weakly basic. The amine group will undergo hydrogen bonding with the silanol groups of the silicate framework and its weak basicity may promote a slightly higher degree of TEOS condensation. When the micelle's shape has transformed to the elongated planar shapes necessary for the formation of the lamellar phase structure, a slightly faster silicate condensation rate occurs and thus a greater extent of the inorganic silicate network may lock in the entire film mesostructure before the micelle has the chance to change its shape to form other mesophases during the film-formation process. Recent reports of an in situ X-ray diffraction study of mesostructured CTAB−silica film formation during dip-coating add support to this argument.[28,29] The sol composition used in that study was very similar to ours but without the addition of THF and organic additives. In the water-rich regime, or late stage, of the film-formation process 2-d hexagonal, 3-d hexagonal, and lamellar phases coexist. Then these phases transform to a cubic phase at the final stage of the process. In our study, locking-in of the lamellar micellar structures during this dynamic evolution of surfactant phases by a greater extent of silicate condensation may be important for the formation of final lamellar mesostructure in the films. Use of a more basic amine is undesirable; addition of a few drops of much more basic aliphatic amines such as diethylamine leads to gelation of the sol within minutes. The ability of carbazole and diphenylamine to cause dramatic film mesostructures may be due to their unique structure and functionality. Other molecules of similar structures and functional groups may eventually be discovered for such effect.

Summary

The structure and the long-range order of silicate thin films templated by surfactants is sensitive to organic dopant molecules and cosolvents. The most striking effect is caused by carbazole. Increasing the mole ratio of carbazole to surfactant by only a few hundredths of a percent (from 0.41 to 0.44) causes a structural change from 2-d hexagonal to lamellar with a very high degree of long-range order. Many dopants require cosolvents to make them miscible in the sol from which the mesostructured film is pulled. Two common cosolvents,

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THF and benzene, also affect the structure at very high concentrations, but for THF at most only a mixture of phases is produced. Fluorene, a planar molecule with almost the same structure as carbazole with the exception of the amine functional group, also causes a change in the film's structure but only at much higher concentrations. Diphenylamine, a non planar molecule similar to carbazole, is effective at changing the structure, but diphenylmethane, a non planar molecule similar to fluorene, is not effective. The cause of the change in the films' structures is attributed to two effects: modifications in the effective shapes of the micelles, and subtle local effects on the hydrolysis and condensation reaction rates caused by the basic aromatic amine functional group.

The effects of dopant molecules on mesostructure provide both problems and benefits. The problems arise when a specific dopant is chosen in order to introduce a desired functionality in the structured film (e.g., optical properties such as luminescence or laser action, photoinduced properties such as electron transfer, or catalytic activity). The delicate balance between the type of structure and the concentrations of the dopants must be monitored carefully in order to make the desired material. The benefits include the ability to design materials with desired structures and mesostructure dimensions (lattice spacings) by the selective addition of dopants. The latter provide new opportunities to deliberately design mesostructured materials for both function and structure.