

Direct Deposition of Mesoscopically Assembled Dye-Doped Silica Films from Aqueous Solutions of Silicon Alkoxides

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Silica films incorporating organic dyes, such as Rhodamine B and Disperse Red 1, were directly deposited on a substrate from aqueous solutions of phenyltriethoxysilane (PhTES). The organic dyes were homogeneously dispersed and firmly trapped in a silica matrix. The X-ray diffraction patterns indicated that the dye-doped films have a mesoscopically assembled structure. Since the period of the mesostructure, ca. 12 Å, was almost the same as the average distance between the dye molecules, the dye-doped films were suggested to be formed by assembling micelle-like clusters consisting of a monomer of the organic dyes surrounded with the hydrolyzed silica precursors. Thus, the monomers of the dyes were tightly captured in a three-dimensional cage of the silica network. Mesoscopically porous silica films were obtained by calcination of the deposited films.

Introduction

Dye-doped organic polymers have been investigated as a wide variety of functional materials. However, their potential applications are limited because organic polymers are generally lacking in chemical and thermal stability and photostability. On the other hand, incorporation of organic dyes into durable inorganic matrixes offers promising prospects for preparation of completely new materials. These materials have attracted much attention commercially as well as scientifically because of their unique properties and their hybrid nature. Such hybrid materials would appear to have potential applications as nonlinear optical materials, chemical sensors, color filters, laser materials, and luminescent solar concentrators.^{1,2}

Many methods have been demonstrated for synthesis of the dye-doped inorganic materials. In particular, the sol-gel method using silicon alkoxides is a well-known technique for incorporating optically active dyes into silicate systems without challenging the rather poor thermal stability of these organic dyes.^{3–11} However, the sol-gel method requires a heat-treating process to

obtain a dense structure and to remove residual organic solvent. Thus, it is relatively difficult to obtain highly dense and durable products containing organic dyes by this method. Moreover, the doped organic dyes are uncertainly released and easily aggregated because of loose incorporation with the host materials. Organic-dye-doped silica films have also been prepared by a deposition method using supersaturated fluorosilicate solutions containing dyes.^{12,13} This method attracts considerable interest as a processing technique to prepare dye-doped dense films at relatively low temperatures. However, incorporation of hydrophobic organic molecules into silica films is difficult because silica matrixes prepared by this method show strong hydrophilic properties. Moreover, this method has the disadvantage of using corrosive hydrofluoric acid.

Recently, silica films containing organic groups were reported to be directly deposited on complex shapes and a wide variety of substrates from aqueous solutions of alkoxides.¹⁴ We found that the organic/inorganic composition of the films could be controlled by the deposition conditions and proposed a mechanism of the film deposition.^{15,16} By this deposition method using alkoxide solutions, silica films containing even hydrophobic dyes were easily prepared on various kinds of substrates. Thus, this method is one of the excellent

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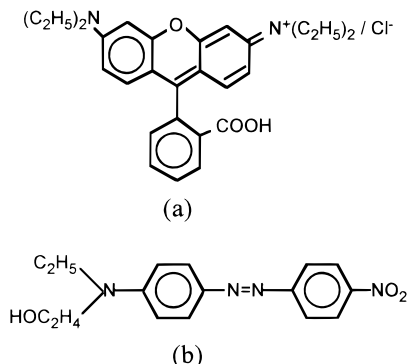


Figure 1. Representation of organic dye molecules incorporated into silica films. (a) Rhodamine B and (b) Disperse Red 1.

Table 1. Typical Compositions of Precursor Solutions for the Sol–Gel Method

material	molar ratio
organic dyes (RB,DR)	~0.1
PhTES	1.0
C ₂ H ₅ OH	2.0
(CH ₃) ₂ NCH	1.8
H ₂ O	5.2
HCl	1.0

candidates for preparation of advanced materials used in a wide range of applications. Moreover, the dye-doped deposited films were found to have a unique structure and desirable properties. In this paper, we report on the new deposition method using aqueous solutions of silicon alkoxide for preparation of silica–organic films incorporating organic dyes. We also describe the properties and the microstructures of the organic-dye-doped silica films prepared by direct deposition.

Experimental Section

Phenyltriethoxysilane (PhTES, C₆H₅Si(OC₂H₅)₃) was used as a starting material. Organic dyes, such as hydrophilic Rhodamine B (RB) and hydrophobic Disperse Red 1 (DR 1) (Figure 1), were added to aqueous solutions of PhTES. The mixture was vigorously stirred at 60 °C for 1 h. The obtained homogeneous solution was mixed with various amounts of hydrochloric acid (HCl) or aqueous ammonia to adjust the pH. The concentrations of PhTES and the organic dyes were varied over 0.03–0.1 and 5 × 10⁻²–5 × 10⁻⁵ mol/L, respectively. After the precursor solutions were stirred again at 60 °C for 1 h, substrates were immersed in the solutions. Glass slides and silicon wafers were used as a substrate. The solutions with the immersed substrates were held in an oven at 60 °C for several hours. The deposited films were ultrasonically washed with pure water to remove loosely bound precipitates. The dye-doped films were dried at 60 °C for 30 min in air. Calcination of the films was carried out at temperatures below 500 °C for 1 h in air.

Dye-doped films were also prepared by a conventional sol-gel method to compare with the deposited films. Sol-gel silica films incorporating organic dyes were prepared as follows: an organic dye (DR 1 or RB) was added to a mixture of PhTES, ethanol (EtOH), and *N,N*-dimethylformamide (DMF). The well-stirred solution and a HCl aqueous solution were allowed to hydrolyze for 1 h at room temperature. DMF was used as an organic solvent to obtain homogeneous films. A typical sample composition is given in Table 1. Spinning was performed to prepare a thin film on a substrate. The obtained films were dried at 60 °C for 30 min in air.

The surface morphology of the films was observed with a scanning electron microscope (SEM) (JEOL JSM-5200) and an

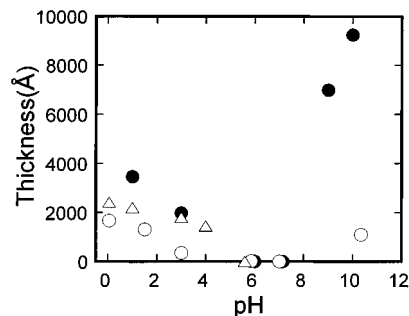


Figure 2. Relationship between film thickness and pH of the precursor solutions. The thickness was estimated by the absorption intensity in FTIR spectra and SEM observation on a cross section of the deposited films. (●) RB-doped films, (△) DR 1-doped films, and (○) undoped films (deposition conditions: DR 1 or RB, 5 × 10⁻³ mol/L; PhTES, 0.03 mol/L; 24 h).

optical microscope (Nikon EPIPHOT-TME). The films were also characterized by Fourier transform infrared (FTIR) spectroscopy (BIO-RAD Digilab Division FTS-65) and X-ray thin film diffraction (XRD) (Rigaku Denki RAD-RC). Optical absorption measurements were carried out for the organic-dye-doped films and the precursor solutions with an ultraviolet–visible (UV–vis) spectrometer (Shimadzu UV-2500PC). The leachability of dyes in the films was evaluated by a decrease in the visible absorbance of the films with immersion in pure water at 60 °C. To examine the orientation of the dye molecules in the matrixes under a high electric field, second-harmonic generation (SHG) was measured using DR 1-doped films. DR 1 is generally known to have a high nonlinear optical coefficient. A high electric field (10 kV) was applied across the film at 150 °C by a corona poling method.¹⁷ After an interval, the film was slowly cooled to room temperature and the electric field was removed. The baseline SHG susceptibility of the poled films was obtained by the Maker-fringe technique.¹⁸

Results

Clear and homogeneous solutions were obtained after mixing PhTES and water at PhTES concentrations of 0.03–0.1 mol/L and across the entire pH range in this study. Precursor solutions containing a hydrophilic dye, such as RB, were clear and homogeneous. A hydrophobic dye, such as DR 1, was also homogeneously dissolved in the aqueous solutions of PhTES below pH 7, although it was not clearly dissolved in aqueous solutions of tetraethoxyorthosilane (Si(OC₂H₅)₄) and methyltriethoxysilane (CH₃Si(OC₂H₅)₃). Hence, PhTES is an excellent starting material for doping both hydrophilic and hydrophobic organic dyes into silica matrixes. Thin films were deposited by immersing substrates into the precursor solutions. The deposition rate and the morphology of the films were influenced by the pH value of the solutions. The pH 4–7 solutions were clear and stable for several months. Figure 2 shows the thickness of the deposited films as a function of the pH value of the precursor solutions with and without dyes. Thin films were deposited on substrates from the precursor solutions at pH below 4 or above 8. This tendency was not affected by the presence of organic dyes in the solutions. However, the deposition rate in the dye-containing solutions was greater than that without the dyes. Figure 3 shows a SEM photograph for the RB-doped film

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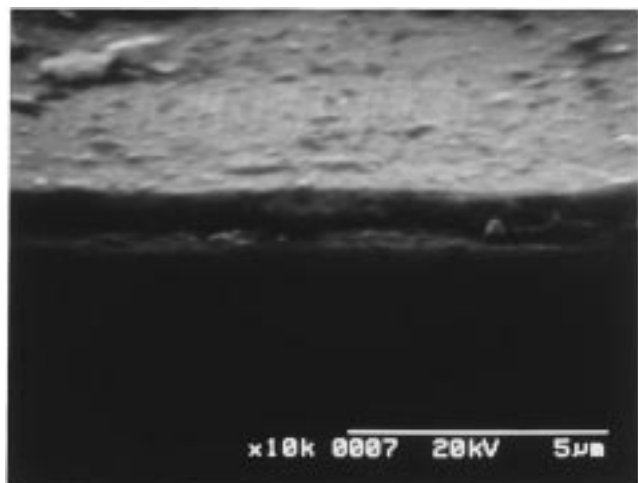


Figure 3. SEM photograph of a deposited silica film incorporating RB.

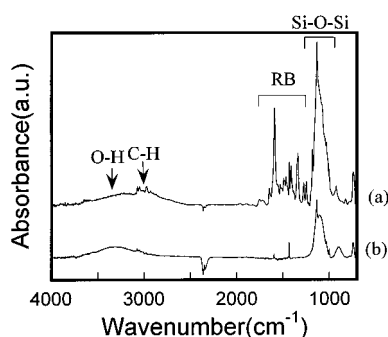


Figure 4. FTIR spectra for silica films deposited from a 0.03 mol/L PhTES aqueous solution at pH 3 for 24 h. For RB-doped films, RB concentration was 5×10^{-3} mol/L. (a) RB-doped silica films and (b) undoped silica films.

deposited from the precursor solution (PhTES, 0.03 mol/L; RB, 5×10^{-3} mol/L; pH 3) for 120 h. Films with a smooth surface were formed under these deposition conditions. The surface of films deposited at pH 3 was flat and homogeneous. At pH below 3, however, dye-doped films have a protuberant surface. We will mainly describe the homogeneous films from solutions with a PhTES concentration of 0.03 mol/L and a pH of 3, unless otherwise indicated.

Figure 4 shows FTIR spectra of the RB-doped and undoped films. For the undoped films, absorption bands splitting into two strong peaks at about 1130 and 1070 cm^{-1} are attributed to asymmetric Si–O–Si stretching vibrations for the phenyl silicates.¹⁹ A sharp band at 1423 cm^{-1} is assigned to monosubstituted benzene ring stretching vibrations of the phenyl group on silicon (Si–C₆H₅) and is accompanied by a band at 738 cm^{-1} which arises from the wag of C–H bonds adjacent to a Si–C bond for Si–C₆H₅.^{20,21} A very weak band at 1562 cm^{-1} is also assigned to the benzene ring stretching vibration. A broad absorption band around 3400 cm^{-1} is due to a stretching vibration of O–H. Absorption bands between 1200 and 1800 cm^{-1} for the RB-doped films (Figure 4a)

are caused by the presence of RB molecules in the films. The intensity of the absorption peaks corresponding to Si–O–Si bonds around 1130 cm^{-1} for the RB-doped films was greater than that for the undoped ones which were formed under the same deposition conditions. This result also means that the deposition rate in the dye-containing solutions was greater than that in the solutions without the dyes.

Figure 5 shows photographs of films deposited from precursor solutions containing various concentrations of the dyes. The organic dyes seemed to be homogeneously dispersed in the deposited films. The UV–vis absorption spectra for the precursor solution and the deposited films are shown in Figure 6. Since the spectra for the precursor solutions and the deposited films are almost the same, the dispersion of the organic dyes in the deposited films is microscopically homogeneous, as in the solution. Since the absorption peak at 556 nm and the shoulder peak at 515 nm in Figure 6a are attributed to RB monomer and dimer, respectively,⁶ the dimer/monomer ratio of RB was estimated with the area of the absorption peaks. Figure 7 shows the absorption spectra for the sol–gel films and the deposited films with various RB concentrations. The dimer/monomer ratio for the sol–gel films was significantly increased with increasing RB concentration (Figure 7a). On the other hand, the dye in the deposited films mainly exists as a monomer regardless of the deposition conditions because the ratio of the deposited films was hardly changed with the RB concentration (Figure 7b). The absorbance of the dye for the deposited films increased linearly with the film thickness. This suggests that the density of the dye molecules in the films was constant regardless of the dye concentration of the precursor solutions. The RB and DR 1 densities in the deposited films were estimated about 5.9×10^2 and 7.6×10^2 mol/m³, respectively. The average distance between the dye molecules was calculated to be ca. 13–14 Å.

A broad diffraction peak around 7° corresponding to a d value of ca. 12 Å was observed for the DR 1- and RB-doped deposited films, as shown by traces c and d in Figure 8. The d value is almost the same as the average distance between the dye molecules estimated from the absorption intensity. In contrast, the XRD patterns for the RB-doped sol–gel films and the undoped deposited films showed no diffraction peaks in the low 2θ range (Figures 8, traces a and b). After combustion of the organic components by heat treatment at 300–500 °C, the broad diffraction peak was also observed and shifted slightly to a lower angle (Figure 8, trace e).

Figure 9 shows changes in the visible absorption peak due to RB in the deposited films and the sol–gel films after a dye-leaching test. The decrease in the absorbance means that the dye was leached from the film into water. The absorbance for the sol–gel films was remarkably decreased in a short time, and nearly half of the dye was leached out over 24 h. On the other hand, dye leaching from the deposited films was hardly seen. This result suggests that the dyes in the deposited films were strongly captured by the silica network compared with those in the sol–gel films.

The Maker-fringe pattern over the angular range $-60^\circ \leq \theta \leq +60^\circ$ is shown in Figure 10. The result is

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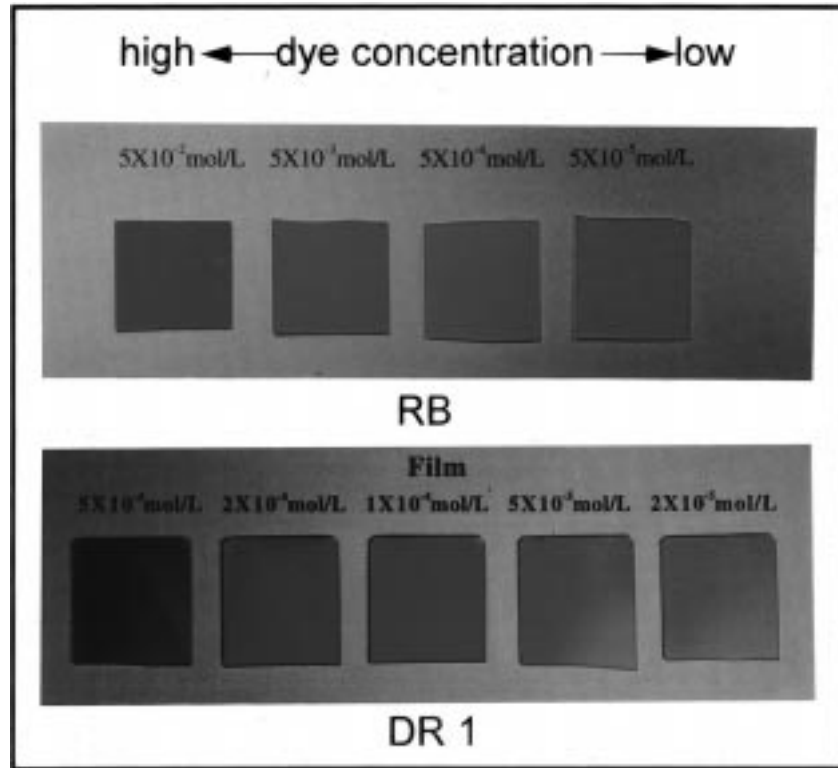


Figure 5. Photographs of silica films deposited in precursor solutions containing various concentrations of RB and DR 1.

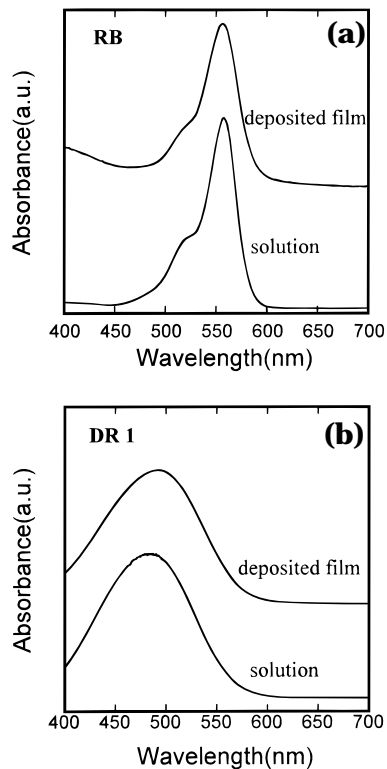


Figure 6. Absorption spectra of RB- and DR 1-doped silica films and the precursor solution. Preparation conditions: pH 3; concentration of PhTES, 0.03 mol/L; concentration of DR 1, or RB, 5×10^{-4} mol/L; deposition time, 24 h (a) RB and (b) DR 1.

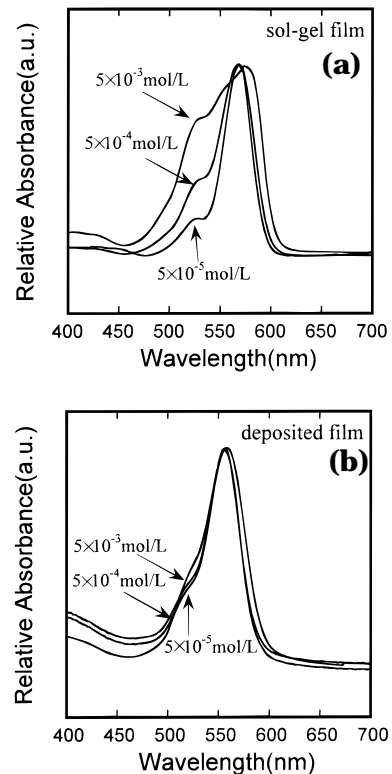


Figure 7. Absorption spectra of silica films with various RB concentrations. (a) Sol-gel films and (b) deposited films. Preparation conditions for deposited films: pH 3; concentration of PhTES, 0.03 mol/L; deposition time, 24 h.

a comparison of recorded SH signals for the deposited and the sol-gel silica films containing DR 1. The SH signal was only observed in the sol-gel films. The result indicates that the DR 1 molecules in the sol-gel

films were orientated under an electric field during the poling process. On the other hand, the SH signal in deposited films was scarcely observed, indicating that DR 1 molecules cannot be rotated in the films.

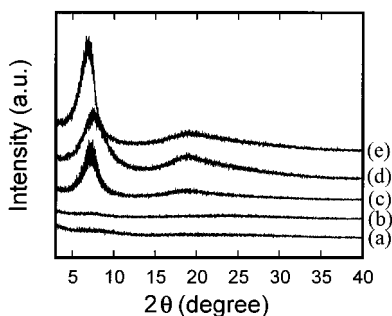


Figure 8. X-ray diffraction patterns for the silica films. (a) Sol-gel with RB, (b) film deposited without dyes, (c) film deposited with DR 1, (d) film deposited with RB, and (e) film deposited with RB and calcined at 500 °C for 1 hour.

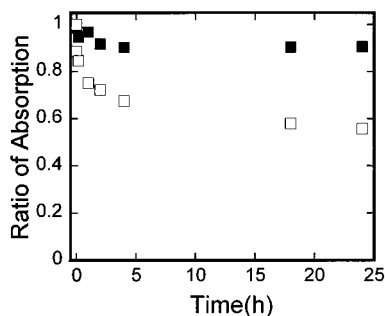


Figure 9. Ratio of the absorption intensity at 560 nm for silica films incorporating RB after and before immersion in water. (■) deposited films with 5×10^{-4} mol/L RB and (□) sol-gel films with 5×10^{-4} mol/L RB.

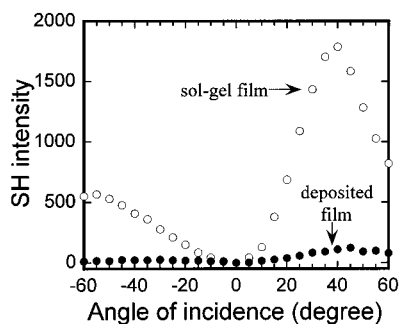


Figure 10. Maker-fringe patterns of deposited films and sol-gel films.

Discussion

Silica films containing organic groups were reported to be directly deposited from aqueous solutions of alkoxides containing methyl and phenyl groups.¹⁴ The completely hydrolyzed alkoxides in the solutions were suggested to be polymerized on substrates through heterogeneous nucleation in an acidic or a basic condition. Since the condensation reaction of the hydrolyzed alkoxides is promoted by a nucleophilic substitution mechanism, the electron-donating property of methyl and phenyl groups coupled to Si atoms is considered to retard the polymerization of the precursors. Thus, the completely hydrolyzed alkoxides are very stable in aqueous solution over the neutral pH range as shown in Figure 2. Deposition is induced in the pH ranges below 4 and above 8 because the condensation reaction of the hydrolyzed alkoxides is catalyzed by H^+ and OH^- . This mechanism is not influenced by the dyes.

Relatively hydrophilic RB was clearly dissolved in aqueous solutions of $Si(OC_2H_5)_4$, $CH_3Si(OC_2H_5)_3$, and

PhTES, in which the alkoxides were considered to be completely hydrolyzed. On the other hand, hydrophobic DR 1 was dissolved only in aqueous solutions of PhTES. The hydrophobic dye molecules in the solutions are assumed to be surrounded by phenyl groups of the hydrolyzed PhTES. Since a phenyl group is more hydrophobic than $-OC_2H_5$ and methyl groups, the PhTES is a more effective amphiphilic agent than the other alkoxides. Thus, silicon alkoxides containing phenyl groups can be utilized as a starting material for preparation of both hydrophilic and hydrophobic dye-doped silica films. A micelle-like cluster consisting of an organic dye and hydrolyzed PhTES, shown in Figure 11a, is presumed to be dissolved in the aqueous solutions. Although RB is a hydrophilic dye, the molecule consists of not only hydrophilic parts but also hydrophobic ones, such as alkyl chains and an isolated benzene ring. Thus, the dye molecule is coordinated with "hydrophobic" phenyl groups and "hydrophilic" hydroxyl groups of the hydrolyzed alkoxides. The incorporation of dyes into silica matrixes under a rapid condensation reaction has been reported to be unsuccessful.²² In this study, however, dyes were successfully doped into the matrixes because the organic molecule was firmly trapped in the micelle-like cluster. An increase in the deposition rate with addition of the dyes (Figure 2) is assumed to be due to the formation of the cluster. Since the solubility of such a large-size molecule is relatively low, the degree of supersaturation for the cluster is higher than that for the hydrolyzed alkoxides without the dyes. Therefore, the addition of the dyes accelerates the film deposition. The dye molecules are suggested to be captured as a monomer with the hydrolyzed alkoxides in the solution. Thus, the dyes were microscopically dispersed in the silica matrixes through the polymerization of the clusters (Figure 11b). This assumption is supported by the result that the dye monomers were dominant in the deposited films according to the visible absorption (Figure 6). Dimerization of RB in the deposited films was scarcely observed regardless of an increase of the dye concentration. This result suggests that the aggregation of the dyes is difficult in the deposited films because the dye molecules are properly trapped in a cage of hydrolyzed silica precursors. On the other hand, the aggregation of the dyes in sol-gel-derived films easily proceeds with an increase of the dye concentration as shown in Figure 7 and as reported in reference 6.

In the XRD patterns for the RB- and DR 1-doped films (Figure 8), a broad diffraction peak around 7° corresponding to a d spacing of ca. 12 Å was observed. On the other hand, the undoped films and the RB-doped sol-gel films showed no diffraction peaks in the low-angle region. These results indicate that the mesoscaled structure was formed during the deposition process with the dyes. Recently, a new family of self-assembled mesoporous materials with well-ordered mesopores has been reported.^{23–26} Hexagonal, cubic, lamellar, and partially ordered mesophases are assigned for these

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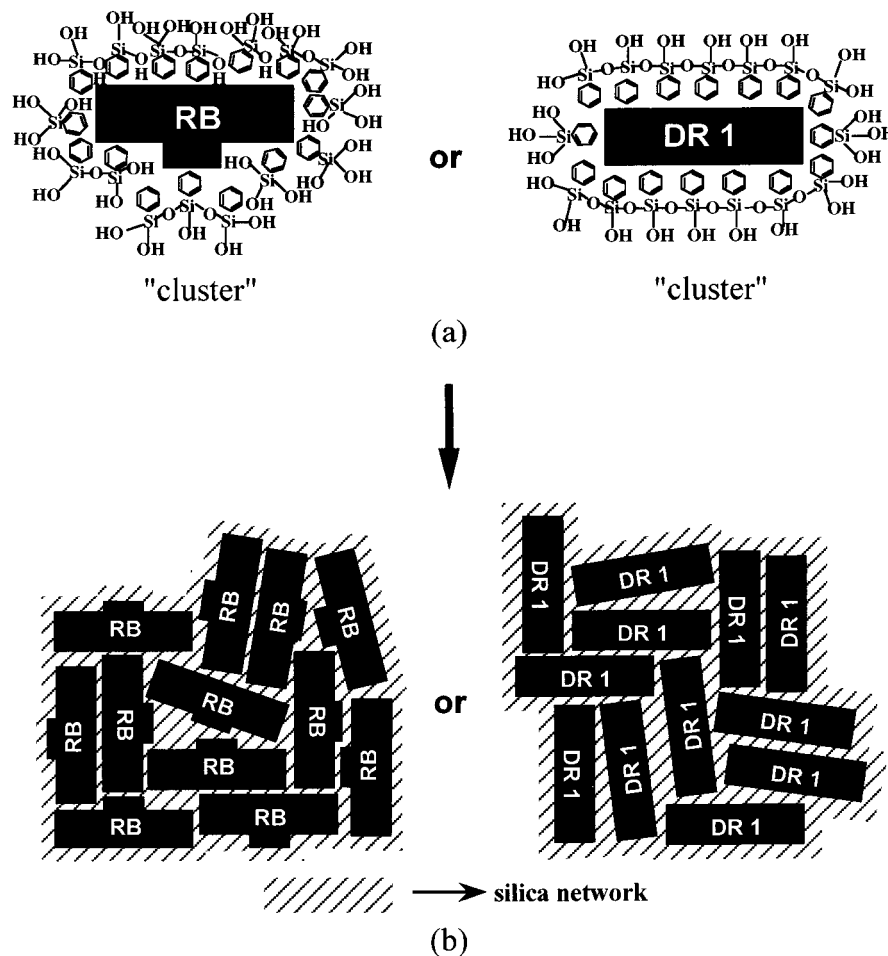


Figure 11. Schematic model for assembly of a micelle-like cluster consisting of a monomer of the dyes and the hydrolyzed PhTES.

materials.²⁵ These phases showed a particular diffraction peak in the low 2θ range of XRD patterns. The XRD pattern for vanadium oxide having a random mesostructure²⁶ is similar to that of the dye-doped deposited films. Thus, the deposited films are suggested to have partially ordered mesostructure. Such meso-scaled ordering is assumed to be formed by assembling the micelle-like cluster consisting of the dyes and the hydrolyzed PhTES as shown in Figure 11b. The density of the dye molecules in the deposited films was calculated to be nearly constant regardless of the deposition rate and the dye concentration of the precursor solutions. The average distance between the molecules was approximately the same as the d spacing. These facts strongly support the notion that the deposited films consist of a periodic mesostructure which was formed by assembling the micelle-like clusters. The size of the dye molecules is important for the estimation of the periodic structure. The largest and the smallest lengths of the dyes are ca. 16 and ca. 5 Å, respectively. Since the period of the mesostructure, ca. 12 Å, is smaller than the largest length of the dyes, complicated assembly of the clusters as shown in Figure 11b is assumed to occur in the films. The partially ordered mesostructure of the films may be due to the complicated assembling of the

clusters. The broad diffraction peak in the low 2θ range was also observed for the samples calcined at 300–500 °C. This suggests that the mesopore of the deposited films is maintained after combustion of the organic dyes. The increase in the d value from ca. 12 to ca. 14 Å indicates a slight structural change of the silica network with the calcination.

As shown in Figure 9, RB molecules doped in the deposited films were hardly removed into water, although those in the sol-gel films were easily leached. The dye molecules are suggested to be firmly captured in the silica network of the deposited films. On the other hand, the molecules in the sol-gel films are mainly adsorbed in pores of the films. DR 1 molecules in polymer and sol-gel silica matrixes are orientated by applying a high electric field, resulting in a large SHG signal. However, the SH signal from the DR 1-doped deposited films was rarely observed (Figure 10). This means that orientation of the molecules hardly occurred even with a high electric field. Thus, the dye molecules in the deposited films are properly trapped by the silica matrix. These results also support the notion that the deposited films are formed by assembling the micelle-like clusters.

The morphology of the deposited films is found to be strongly dependent on the deposition conditions. Protuberances appeared on the film surface in the pH range below 3, although a relatively smooth surface was formed at pH 3. The diameter of the protuberances

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increased with a decrease in pH. In the precursor solution with a high dye concentration, the film deposition occurred rapidly and hemispheric protuberant films were formed in the initial stage. The variation of the morphology of the deposited films is assumed to be ascribed to the supersaturation level of the solutions. As described above, the supersaturation level of the solutions is high in the pH range below 3 or at a relatively high concentration of the dyes, resulting in an increase in the deposition rate. The formation of films proceeds with the heterogeneous nucleation on the surface of the substrates and the deposited film. The films formed with a relatively low deposition rate have a smooth surface. At an extremely high supersaturation level, the formation of precipitates through homogeneous nucleation becomes dominant. In the middle range of the supersaturation, the growth of the films is presumed to be controlled by a diffusion process from the bulk solution to the growth surface. In this case, a small unevenness would be promoted because the growth rate at a projected area is relatively high. Thus, protuberances on the film surface are formed under high supersaturation conditions.

Conclusions

Direct deposition of organic-dye-doped silica films using aqueous solutions of silicon alkoxides was investigated. Organic dyes, such as hydrophilic RB and hydrophobic DR 1, were successfully doped in silica

films deposited from aqueous solutions of phenyltriethoxysilane. The morphology and the microstructure of the dye-doped films were strongly dependent on the deposition conditions, such as pH, the concentration of the dyes, and the deposition time. The dye-doped films are deduced to have a partially ordered mesostructure on the basis of X-ray diffraction analysis. The organic dyes doped in the films were homogeneously dispersed as in the precursor solution and were firmly captured in the matrix. These properties of the dyes in the deposited films are essentially different from those in conventionally prepared sol-gel films. Thus, the deposition of the dye-doped films is ascribed to assembly of micelle-like clusters consisting of a dye molecule and hydrolyzed alkoxides on the surface of substrates. The direct deposition using the alkoxide solutions is expected to be a promising synthesis method for various applications of organic-dye-doped films, such as in a luminescence solar concentrator, because the dye molecules are homogeneously dispersed and tightly trapped in the inorganic matrix. This method is also useful to prepare mesoporous silica films with a pore diameter of ca. 14 Å because the partially ordered structure remained after combustion of the organic molecules.

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