Preparation and luminescent properties of Rh6G-doped lamellar, hexagonal, and cubic mesostructured SiO$_2$ waveguides

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Abstract

We successfully fabricated laser dye (Rh6G)-doped lamellar, hexagonal, and cubic mesostructured SiO$_2$ waveguides with a combined method of inorganic/organic co-assembly and soft-lithography. These mesostructured SiO$_2$ waveguide arrays were made on low-refractive index mesoporous SiO$_2$ clad films (the upper cladding is air), and waveguiding was confirmed for all samples. When pumping the waveguides with an excitation light at normal incidence, they exhibited a broad emission peak (yellow in color) below certain pumping intensity (pumping threshold), and above the threshold a sharp emission peak (orange in color) was observed from the end of the waveguides. The gain-narrowing is attributed to amplified spontaneous emission that results from the homogenous distribution of highly doped dye molecules (up to 0.8 mol%) within the organized mesochannels of the arrays. The pumping threshold values for the respective mesostructured waveguides are different from each other, increasing in the order of lamellar, hexagonal, cubic mesostructure.

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1. Introduction

Mesostructured materials prepared by nanotechnology have been attracting lots of attention because nanotechnology allows precise control of the feature and morphology of the mesostructures in the materials [1–3]. Among the nanotechnology, surfactant templating [4,5] and lithography [6,7] are typical ‘bottom-up’ and ‘top-down’ method, respectively, for fabricating novel optical or electronic mesostructured materials. The former method constructs the desired nanostructure by self-assembly of small molecules, and the latter does it by dividing large matters. By the cooperative assembly of inorganic species (metal oxides or metal chlorides) and organic surfactants as structure-directing agents, highly ordered materials with various mesostructures can be easily made [8]. Moreover, these highly ordered mesostructured materials offer a uniform and adjustable environment as a good host for encapsulating guest molecules, thereby leading to highly homogenous distribution of the guest molecules in the host [9]. On the other hand, electron-beam (EB) lithography or photolithography has also been widely used for synthesizing mesostructured materials through fabricating micropatterned resist molds with air cavities on a nano to micrometer length scale [10]. Because these bottom-up and top-down nanotechnologies have their own advantages and disadvantages as well, the combination of these technologies is particularly useful in making novel nanostructured materials, such as hierarchically ordered materials with unique optical or electronic properties.

Yang et al. [11] reported the first hierarchically ordered oxides with three-dimensional (3D) structures patterned over a multiple-length scale by combining micromolding, polymer templating, and inorganic/organic co-assembly; such hierarchically ordered oxides promise potential applications in miniaturized optical and electronic devices. One of the representative examples is the novel mesostructured Rh6G-SiO$_2$ waveguides, which can be fabricated with a combination of acidic sol–gel surfactant templating chemistry and soft lithography [12]. This device has been proved to exhibit amplified spontaneous emission (ASE) with a lower pumping threshold than sol–gel SiO$_2$ glass [13]. However, in previous studies the synthesis of Rh6G-SiO$_2$ waveguides with only hexagonal mesostructure has been reported. Since materials with a lamellar, hexagonal or...
cubic mesostructure have respectively different porosity, mechanical or thermal stability, and dielectric constant etc. [14], a systematic and quantitative investigation on the fabrication, properties, and performance of various self-assembled mesostructures is necessary to use these mesostructured materials in practical applications.

Here, we prepared a highly ordered hexagonal mesoporous SiO2 thin film on a silicon substrate, which serves as a cladding for the present waveguides, by a water vapor hydrothermal treatment method [15]. Then, Rh6G-doped SiO2 arrays with three kinds of mesostructures were synthesized by adjusting the volume ratio of a triblock copolymer template in the precursor solution and then patterned on the SiO2 clad film by soft-lithography. Waveguiding was enabled due to the structure with a high-refractive index of Rh6G-doped mesostructured SiO2 arrays \((n = 1.43)\) sandwiched between two low-refractive index claddings: mesoporous SiO2 film \((n = 1.19)\) and air \((n = 1)\). The photoluminescence (PL) properties of the waveguides and how the PL properties are affected by the mesostructures of waveguides are discussed.

2. Experimental

2.1. Fabrication of Rh6G-doped mesostructured SiO2 waveguides

A highly ordered hexagonal mesoporous SiO2 thin film was synthesized through a lamellar-to-hexagonal phase transformation on a silicon substrate \((2 \times 2 \text{ cm}^2)\). The preparation method was described in our previous paper [15]. Preparation of Rh6G-doped lamellar, hexagonal or cubic mesostructured SiO2 precursor solutions was modified from Ref. [16]. Typically, 2.6 g of tetraethyl orthosilicate (TEOS, 98%, Wako) was hydrolyzed in a mixed solution containing 1.35 g of diluted hydrochloric acid (0.04 wt%) and 3 g of ethanol (EtOH) at room temperature (RT). After 15 min, this hydrolyzed silica solution was mixed with a 2 g of EtOH solution containing substoichiometric amounts of laser dye Rhodamine-6G (Rh6G, Wako) and the poly(ethylene oxide)--poly(propylene oxide)--poly(ethylene oxide) triblock copolymer EO20PO70EO20 (Pluronic P123, BASF). The added amount of P123 for lamellar, hexagonal or cubic was 1.925, 0.7 or 0.356 g, respectively, according to the volume percent of P123 in precursor solutions. The silica/P123/Rh6G precursor solutions were then stirred for 3 h at RT. Finally, Rh6G-doped mesostructured SiO2 waveguides were fabricated by patterning the silica/P123/Rh6G precursor solutions on the highly ordered hexagonal mesoporous SiO2 thin film, which deposited on a silicon substrate previously. Patterning was performed by a soft-lithographic technique (micromolding-in-capillaries; MIMIC) using polydimethoxysilane (PDMS) molds to produce surface replicas of the relief patterns of PDMS [17]. Here, a stripe-patterned PDMS mold was first placed on the highly ordered hexagonal mesoporous SiO2 thin film, a drop of silica/P123/Rh6G precursor solution was placed at one end of the mold, and the line arrays were allowed to fill by capillary flow. The schematic picture of fabricated Rh6G-doped mesostructured SiO2 waveguides is shown in Fig. 1a.

2.2. Characterization

Mesostructures of synthesized SiO2 thin films were identified by small-angle X-ray diffractometry (SA-XRD; Rigaku-Rint 2000, Cu Kα) and transmission electron
microscopy (TEM; Hitachi 800, 200 kV). Thickness and morphology of the Rh6G-doped mesostructured SiO2 waveguides were recorded on a field-emission scanning electron microscopy (FE-SEM; Hitachi S5000). PL measurements were performed using a light source from the second harmonic of a Q-switched Nd:YAG laser (532 nm, 10 ns pulse width, 10 Hz repetition rate), which was passed through an adjustable slit and focused by a rectangular lens onto the sample (2 × 0.4 mm). Emission light was focused and recorded in a 90° set-up on a photonic multichannel analyzer (Hamamatsu PMA-11).

3. Results and discussion

Fig. 1b shows a SEM image of Rh6G-doped mesostructured SiO2 arrays with 1-cm long, 2.5-µm wide, 0.5-µm height, and 2.5-µm space stripe features. We can control the width and space of the arrays by using PDMS molds with different line spaces. The enlarged cross-section SEM image shows the three layers of one array with smooth surfaces (Fig. 1c). The high surface area of the line patterns is essential for achieving low-loss waveguiding.

Patterned Rh6G-doped SiO2 arrays with three kinds of mesostructures can be prepared using P123 as a structure-directing template and adjusting the volume percent of P123 (Φ) in the precursor solution. Fig. 2 shows SA-XRD patterns of ‘as-made’ Rh6G-doped SiO2 thin films with a (a) lamellar, (b) hexagonal, and (c) cubic mesostructure. In this figure, SA-XRD patterns for the respective thin films after calcination at 400 °C (i.e. ‘calcined’) are simultaneously shown. Lamellar structure was synthesized when Φ value was controlled to be 70%. The SA-XRD pattern in Fig. 2a (trace as-made) exhibited as many as five even spaced peaks corresponding to the (001), (002), (003), (004), and (005) reflections of a lamellar structure. These peaks can be divided into two groups: odd peaks (including (001), (003), and (005) peaks) and even peaks (including (002) and (004) peaks), which implies the formation of highly ordered alternating silica/P123 surfactant layers in films [18]. After calcination to remove the surfactant template, only one broad peak remained at larger angle (Fig. 2a; trace ‘calcined’). This significant change of the XRD pattern indicates that the lamellar structure in the film greatly collapsed [19]. The layer-by-layer morphology of lamellar structure was also observed in a TEM image (Fig. 3a). Hexagonal mesostructure was synthesized when the Φ value was adjusted to be 45%. Before calcination, three well-resolved peaks were observed with d-spacings of 100, 49, and 32 Å, which can be indexed as (100), (200), and (300) reflections, respectively, of a 2D hexagonal (p6mm) mesostructure [20]. These peaks shifted only slightly to larger angles after calcination. The only (h00) SA-XRD peaks here demonstrate the pore channels of the film are highly oriented and parallel to the substrate surface [21]. This can also be seen from a plan-view TEM image (Fig. 3b). Cubic mesostructure was synthesized when Φ = 30%. The SA-XRD pattern of cubic structure exhibited two (h00) peaks and shifted slightly after calcination, which is similar with that of hexagonal one (Fig. 2b and c). Therefore, the only method to determine the mesostructure is TEM investigations. The plan-view TEM image in Fig. 3c and diffraction spots in the inset show a well-ordered cubic mesostructure. This TEM image is similar to the one for cubic mesoporous silica SBA-16, whose structure was solved using TEM data.

Fig. 2. SA-XRD patterns of Rh6G-doped SiO2 thin films with a (a) lamellar (b) hexagonal, and (c) cubic mesostructure.
If it is the case, the structure in the present study can be estimated to be a body-center cubic \( \text{Im} \text{3m} \) mesophase oriented with \{100\} lattice planes parallel to the interface. In addition, the reason of why the first peak in the SA-XRD pattern is indexed as the (200) reflection has also been explained at other studies [16].

Because of the refractive index of the Rh6G-doped mesostructured SiO\(_2\) arrays (\( n = 1.43 \)) is higher than that of the mesoporous SiO\(_2\) film underneath (\( n = 1.19 \)) and that of air (\( n = 1 \)), waveguiding can be achieved within the arrays from internal reflection of light at the lower-refractive-index mesoporous SiO\(_2\) film and air interfaces.

Fig. 3. TEM images of calcined SiO\(_2\) thin films show a: (a) lamellar structure along \[001\] zone axis, (b) hexagonal structure along \[110\] zone axis, and (c) cubic structure along \[100\] zone axis. Selected area electron diffraction patterns and the schematic images of mesostructures are also shown in the insets (Bar = 50 nm).

Fig. 4. Emission spectra collected perpendicular to the excitation light along the waveguide axis at (a) low pump intensity (3.01 kW/cm\(^2\); below the threshold) and (b) high pump intensity (14.46 kW/cm\(^2\); above the threshold). Optical images of the emission light from the waveguides recorded with a CCD camera are shown in the insets.

Fig. 5. Output intensity of the Rh6G-SiO\(_2\) waveguides with lamellar, hexagonal, and cubic mesostructures as a function of laser pump intensity.
When the Rh6G-doped mesostructured SiO$_2$ waveguides were pumped with a Nd:YAG laser (532 nm) in a 90° geometry (Fig. 1a), at low intensities below certain pumping intensity (pumping threshold) a broad PL spectra at 566 nm (yellow in color) was observed with a full width at half-maximum (FWHM) of about 60 nm (Fig. 4a). As the pump intensity exceeded the threshold, however, the peak began to narrow and finally a sharp peak at 579 nm (orange in color) with a FWHM of about 7 nm was observed (Fig. 4b). For 0.1 mol% Rh6G-doped lamellar, hexagonal, and cubic mesostructured SiO$_2$ waveguides as an example, a dependence of the output intensity with increasing pump intensity was shown in Fig. 5. From these data, a low threshold of about 9 kW/cm$^2$ was deduced for lamellar mesostructured SiO$_2$ waveguides. The threshold values for hexagonal and cubic ones were found to be 33 and 47 kW/cm$^2$, respectively (Fig. 5). Moreover, the observed gain-narrowing emission was indicative of ASE, a phenomenon that spontaneously emitted light is amplified as it propagates along the waveguide [23,24]. This can only be found in the situation that dye molecules are dispersed homogenously in the host. To confirm this, we varied the excitation length $x$ from the edge apart and detected the FWHM of the emission peak. The results were plotted in Fig. 6. It showed that the gain-narrowing is dependent on the excitation length, which proves its origin as resulting from ASE, not from other factors such as superfluorescence [25]. The emission light can only be detected when the deviation angle of the detector was less than 5° from the edge of the waveguides. The polarization ratio of the emission light parallel to the substrate plane versus normal to the substrate plane was calculated to be about four when pump intensity exceeded the threshold. The output intensity was increased with the concentration of Rh6G increased. The maximum concentration of Rh6G doped in mesostructured SiO$_2$ without quenching was found to be 0.8 mol%.

The synthetic conditions and threshold values for different mesostructured Rh6G-doped SiO$_2$ waveguides are shown in Table 1. At the same Rh6G concentration (0.1 mol%), the threshold value of lamellar mesostructured waveguides (9 kW/cm$^2$) is much less than those of hexagonal ones (33 kW/cm$^2$) and cubic ones (47 kW/cm$^2$). We try to explain this result with two reasons. One is the character of different structures. Lamellar structure can be regarded as an arrangement of plane-by-plane in which molecules are aggregated in 1D ordering. In contrast, molecules in hexagonal or cubic structures are thought to arrange in a form of channels (2D ordering) or a form of cubes with connecting pores (3D ordering), respectively. We assume that the emission light from lamellar mesostructured waveguides (1D ordering) has the least obstacles than from hexagonal (2D ordering) or cubic (3D ordering) ones, thus results in the smallest threshold value. The other reason is that the amount of P123 used to synthesize lamellar structure is more than that to synthesize hexagonal or cubic structure (Table 1). Because P123 can promote dye dispersion, we believe more P123 quantities in lamellar structured waveguides can suppress unfavorable Rh6G-dimerization and lead the mostly isolated Rh6G molecules. However, the photo-stability (lifetime) of lamellar mesostructured waveguides was not as good as that of hexagonal or cubic ones (Table 1). This might be due to the same reason that lamellar mesostructured waveguides have the most amounts of organic P123, which was burned out during the irradiation of excitation pumping.

### 4. Conclusions

We fabricated the Rh6G-doped mesostructured SiO$_2$ waveguides by combining a soft lithographic method (micromolding in capillary) with sol–gel chemistry in

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**Table 1.** Synthesis conditions and photoluminescence properties for the mesostructured SiO$_2$ waveguides

| Mesostructure | $\Phi$ (%) | P123 (g) | $d$-spacing$^a$ (Å) | $d$-spacing$^a$, calcined (Å) | Threshold (kW/cm$^2$) | Photostability (pulses) |
|---------------|------------|----------|---------------------|-----------------------------|----------------------|------------------------|
| Lamellar      | 70         | 1.925    | 100                 | 22                          | 7–9                  | 800                    |
| Hexagonal     | 45         | 0.700    | 100                 | 59                          | 30–33                | 2300                   |
| Cubic         | 30         | 0.356    | 98                  | 66                          | 45–47                | 2700                   |

$^a$ The $d$-spacing of the first peak in the diffraction pattern of Fig. 2.
the presence of P123 as templates. Three kinds of mesostructures (lamellar, hexagonal, and cubic) were synthesized and characterized by SA-XRD and TEM. When pumping the waveguides in a 90° geometry, ASE from the waveguide edge was observed. The ASE was resulted from a concentrated (up to 0.8 mol%) and homogenous Rh6G distribution. Rh6G-doped lamellar mesostructured SiO2 waveguides exhibited the lowest threshold value but the weakest photostability than hexagonal and cubic ones. This might be due to the structural character and the amounts of surfactant contained in the different mesostructure. The Rh6G-doped mesostructured SiO2 waveguides presented in this study are promising as potential materials for optical applications.

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