Patterning and optical properties rhodamine B-doped organic–inorganic silica films fabricated by sol–gel soft lithography

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Abstract

Rhodamine B (RB)-doped organic–inorganic silica films and their patterning were fabricated by a sol–gel process combined with a soft lithography. The resulted film samples were characterized by atomic force microscope (AFM), optical microscope and UV/Vis absorption and photoluminescence excitation and emission spectra. The effects of the concentration of the RB dye and heat treatment temperature on the optical properties of the hybrid silica films have been studied. Four kinds of patterning structures with film line widths of 5, 10, 20 and 50\,\textmu m have been obtained by micromolding in capillaries by a soft lithography technique. The RB-doped hybrid silica films present a red color, with an excitation and emission bands around 564 and 585\,nm, respectively. With increasing the RB concentration, the emission intensity of the RB-doped hybrid silica films increases and the emission maximum presents a red shift. The emission intensity of the films decreases with increasing the heat treatment temperatures.

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1. Introduction

The incorporation of organic dyes into solid matrices is attracting wide interest because of useful applications as light concentrators in solar cells, optical waveguides, laser materials, sensors and nonlinear optical materials\cite{1–6}. The low synthesis temperature of the sol–gel method allows the incorporation of soft dopants such as organic molecules, without damage to their molecular structure. The embedding of molecules in a rigid matrix leads to isolation of the active species that hinders intermolecular interaction and intramolecular rearrangement, protects the active molecule from the environmental attack and/or photofragmentation and increases the life of the material\cite{7}.

On the other hand, patterning of films plays an important role in sensors, integrated optical elements
for switching, waveguides and light amplification devices [8,9]. There are many methods for patterning of sol–gel films, such as laser patterning method [9], photochemical method (for photosensitive sol–gel films) [10], and traditional photolithographic method [11,12]. All of these methods have their own advantages and limitations. Recently, much attention has been paid to nonphotolithographic patterning techniques collectively known as soft lithography, which have the potential of becoming versatile, and low cost methods for creating micrometer and sub-micrometer size structures [13]. So far, many reports describing the use of soft lithography to fabricate patterned structure can be found in the literature [14–16]. In this paper, we report the sol–gel synthesis of Rhodamine B (RB) dye-doped organic–inorganic silica films and their patterning via soft lithography (micromolding in capillaries), and investigate the optical properties of the films as a function of the dye concentration and the densification temperature.

2. Experimental

2.1. Preparation of the nonpatterned films

The main starting materials used for the preparation of the film samples were the silane coupling agent 3-glycidoxypropyl trimethoxysilane (GPS, C. P., Gaizhou Chemical Plant, Liaoning), tetraethoxysilane Si(OC2H5)4 (TEOS, C. P., Beijing Chemical Plant) and organic dye Rodamine B (A. R.). The coating solution for film deposition was obtained by two steps. First, mix the GPS with the ethanol solution of RB with continuous stirring for at least 10 h. Then TEOS and H2O, together with several drops of concentrated HCl, were added into the obtained solution. The solution was stirred for about 20 h. The final molar ratio of TEOS/EtOH/H2O/GPS was 1:18:4:1. The RB concentration in the starting liquid solution varies from 1×10^{-3} to 5×10^{-3} M.

Thin films were prepared by depositing the above sol on general silicate glass substrates via dip-coating technique. Before deposition, the glass substrates were thoroughly ultrasonicated in ethanol solution of KOH for 15 min, washed with distilled water. The cleaned substrates were dipped into the coating solution, then withdrawn from the solution at a speed of 0.5 cm s^{-1}. The film samples were then baked at 60–270 °C for 2 h for densification. The obtained films have a thickness of 268 nm and a refractive index of 1.156.

2.2. Patterning of the films

The patterning of the phosphor films was carried out by soft lithography as described previously [14–16]. First, polydimethylsiloxane (PDMS) stamp...
modes were fabricated by casting PDMS on masters having desired patterns. In a typical experimental procedure, we placed a master in a glass petri-dish, and poured a 10:1 (v/v) mixture of SYLGARD silicone elastomer 184 and its curing agent (Dow corning) over the master. The elastomer was degassed for approximately 30 min at room temperature, cured at 65°C for about 4 h, and then peeled gently from the master. In this way, the PDMS modes with different channel widths (5–50 μm) were obtained.

The PDMS modes were placed in conformal contact with thoroughly cleaned silicon wafer substrates. The silicon oxide layer on the surface of silicon wafer can be used as a buffer layer. The channels of the mode thus formed capillaries with the silicon wafer substrate. The above sol for dip-coating was then dropped at the open end with a transfer pipette. The capillary force made the sol

Fig. 2. Optical micrographs of the patterned Rodamine-doped silica films. (a) Line widths = 5 μm, (b) 10 μm, (c) 20 μm, (d) 50 μm.

Fig. 3. Absorption spectra of silica films doped with different contents of RB.
flow into the mold. Then the modes and substrates were dried at 100°C overnight. After careful removing the modes, the patterned gel films were obtained.

2.3. Characterization

The UV/Vis absorption spectra for the films were measured on a TU-1901 spectrophotometer. Photoluminescent excitation and emission spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The thickness and refractive index of the transparent nonpatterned film was measured on a AUEL-III automatic laser ellipsometer. The morphology of the films was studied by a nanoscope III atomic force microscope (AFM) with a tapping mode (Digital Instruments). The patterning pictures were taken on a Leica DMLP optical microscope. All of the above measurements were performed at room temperature (RT).

3. Results and discussion

3.1. AFM and optical micrographs

The RB-doped organic–inorganic silica films present a red color. The morphology of film deposited on silicate glass substrates (transparent single layer) was investigated by AFM. Fig. 1 shows the AFM images of RB-doped SiO2 films after heat treatment at 120°C. The grain structures of the film can be seen clearly from planar image of Fig. 1(a), and the particles have a size of 30–50 nm with an elliptic shape. The stereo image in Fig. 1(b) indicates that the surface of the film is very smooth with an RMS roughness of 8–10 nm.

Fig. 2 shows the optical micrographs of the patterned films obtained from different micromold channel size. The dark and white regions in the figures correspond to the silica film bands and blank spaces, respectively. It can be seen clearly that the silica film bands are uniform in width and crack free. Four kinds of film band width with equal space have been obtained, i.e., 5, 10, 20 and 50 μm as indicated in the Table.
Fig. 2(a,b,c,d), respectively. The maximum length of the patterned structures is about 1 cm. These results demonstrate that the sol–gel films can be successfully patterned by the soft lithography technique as observed previously [15,16], which are promising for optical applications.

3.2. Optical properties of the films

The patterned and nonpatterned RB-doped silica films show similar optical properties. So all the characterizations for the optical properties were performed on the nonpatterned films due to their relatively easy availability.

3.2.1. Concentration effects of RB

The sol solutions with different dye concentration in the range $1 \times 10^{-3}$–$5 \times 10^{-3}$ mol/l were prepared to check the effects RB dye concentration on the optical properties of the films. Fig. 3 shows the absorption spectra of the RB-doped silica films in the visible region. Independent of the concentration of RB, the absorption spectra consist of a strong absorption band with a maximum at 564 nm with a shoulder around 526 nm. Note that the absorption intensity of the films increases with increasing the concentration of RB.

The main 564-nm absorption band is due to the rhodamine B monomer, while the shoulder around 526 nm is from the rhodamine B dimer [17]. The excitation spectra of RB-doped silica films are very similar to the absorption spectra, i.e., a strong excitation band is observed at 564 nm with a shoulder at shorter wavelength 525 nm, which are due to RB monomer and dimer, respectively, as shown in Fig. 4(a).

The emission spectra of the silica films doped with different concentrations of RB are shown in Fig. 4(b). Only a single emission band with a maximum between 581 and 592 nm is observed depending on the concentration of RB. This emission is from RB monomer [18]. Clearly, the emission intensity of the RB-doped silica films increases with the increase of RB concentration from $1 \times 10^{-3}$ to $5 \times 10^{-3}$ mol/l. No concentration quenching effect was observed in the studied RB concentration range. Additionally, a red shift for the emission band can be observed from low RB concentration to high RB concentration. This may be caused by two factors. First, it may be due to the changes of the environment of dye molecules such as polarity or polarizability. The silica matrix is not expected to change much upon increasing the dye concentration, but the number of dye molecules that are in each others vicinity increases. This leads to interactions between neighboring molecules, which lowers their excited state energy and produces a red shift in the spectra, as observed previously [19]. Secondly, a self absorption process could also be responsible for the observed small red shift in the emission band. With the increase of RB concentration, the self absorption of RB will increase, which leads to the red shift of the emission band.

3.2.2. Temperature effects

The emission spectra of RB-doped silica films have been studied as a function of heat treatment temperatures, which is shown in Fig. 5. From Fig. 5, it can be seen that with increasing the heat treatment temperature from 60 to 270 °C, the shape of the emission spectra of RB-doped silica films remains unchanged, but the emission intensity decreases gradually and completely quenches after 270 °C.

RB is a kind of xanthene dye, whose optical properties depends on many factors, such as solvents (polarity and aprotic character), concentration, pH value, etc. [20–23]. Generally, it has three molecular forms:

In a polar solvent, such as ethanol, the carboxyl groups participates in a typical acid–base equilibrium $\text{RBH}^+ = \text{RB}^+ + \text{H}^+$. Forms (a) $\text{RBH}^+$ and (b) $\text{RB}^+$ are strongly colored and emissive. However, the lactone form (c) is colorless and shows no emission because the $\pi$-electron system of the dye chromophore is...
interrupted [20]. With the increase of the densification temperature, form (a) RBH + and (b) RB F will transform to lactone form (c) to some extent, and furthermore, RB dye will decompose at even higher temperature. Thus, it is understandable that the emission intensity of RB-doped silica films decreases with the increase of heat treatment temperature. Furthermore, with the increase of heat treatment temperature, the hybrid silica gel matrix will be more densified. This will decrease the distance between RB molecules, which could cause additional self-quenching for the luminescence of RB.

4. Concluding remarks

Rhodamine B-doped organic–inorganic silica films have been successfully prepared by a sol–gel dip-coating process, and these films can be patterned into film bands from 5 to 50 μm by a soft lithography technique (micromolding in capillaries). The absorption and emission intensity of the RB-doped silica films increases with increasing the RB concentration from 1 × 10⁻³ to 5 × 10⁻³ mol/l, but decreases with increasing the increasing the heat treatment temperature.

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