Influence of deposition time on the morphology and optical properties of SiO₂-ZnO composite photonic crystals

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SiO₂ photonic crystal were successfully prepared by vertical deposition and then used as a template to fabricate SiO₂-ZnO composite photonic crystals on ITO substrates by electrodeposition and subsequent calcination. A number of different deposition times were used. The morphologies of the silica opals and SiO₂-ZnO composite photonic crystals were investigated by scanning electron microscopy. It was found that ZnO particles grew randomly on the surfaces of the silica spheres when the deposition time was short. As the deposition time was increased, the ZnO particles grew evenly on the surfaces of the silica spheres so that the interstitial space of the silica template was filled with ZnO particles. Reflectance spectra of the SiO₂-ZnO composite crystals revealed that all of the fabricated photonic crystals exhibit a photonic band gap in the normal direction.

photonic crystals, electrodeposition, photonic band gap

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Since John [1] and Yablonovitch [2] introduced the ideas of confinement, control of light and spontaneous emission by photonic crystals in 1987, photonic band gap materials have attracted increasing attention from scientists and engineers. Photonic crystals are generally characterized by a periodic dielectric structure which induces opening of the photonic stop bands or band gaps through Bragg diffraction. A promising technique to fabricate 3-D photonic crystals with a photonic band gap in the optical wavelength range is the self assembly of spherical colloidal particles [3]. These colloidal photonic crystals are also known as opals.

There are a great number of methods used to fabricate opal photonic crystals such as vertical deposition [4], two-substrate vertical deposition [5], convective self-assembly deposition [6], and electrophoretic deposition [7]. However, the fabrication of 3-D opal photonic crystals is still a technical challenge, because many kinds of intrinsic defects such as plane defects, line defects, and dot defects appear during self-assembly. During self-assembly, surface charge

on colloidal spheres is a key element in successfully producing high quality colloidal crystals. Some scientists had fabricated SiO₂ photonic crystals with high quality by enhancing surface charge on SiO₂ spheres via modification with succinic acid [8]. In this work, vertical deposition was chosen as the self-assembly method to fabricate SiO₂ photonic crystal templates as it provides a relatively simple approach to obtaining high quality opal films.

Silica or polymer opals do not have a full band gap because of their low refractive index (1.47 for silica). However, these opals are calculated to have a photonic band gap in the (111) direction, so opal-based materials, such as composite photonic crystals with different fillings and inverted opals [9–11], are of interest. ZnO is an important semiconductor material with a wide electronic band gap, which has a higher refractive index (2.1) than other materials. As a result, an increasing number of SiO₂-ZnO composite photonic crystals have been fabricated by a range of methods [12, 13].

In this work, SiO₂-ZnO composite photonic crystals were fabricated by electrodeposition followed by calcination at

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500°C for 2 h. Different deposition times were used during electrodeposition to fabricate SiO₂-ZnO composite photonic crystals.

1 Experimental

(i) Chemicals. Deionized water (analytical purity), anhydrous ethanol (analytical purity), tetraethylorthosilicate (TEOS, analytical purity), ammonia (25 wt%–28 wt%), and Zn(Ac)₂·2H₂O (analytical purity).

(ii) Synthesis of SiO₂ colloidal spheres. SiO₂ colloidal spheres were prepared using the Stöber method [14]. An ethanol solution containing 4.8 mL TEOS and 50 mL anhydrous ethanol was added to a glass reactor containing 7.0 mL ammonia and 3.0 mL deionized water at 30°C. The mixture was stirred with a magnetic stirrer for about 12 h. The chemical reactions describing the hydrolysis and condensation of alkoxysilanes can be summarized as follows:

The obtained SiO₂ colloidal spheres were washed by repeated centrifugation and ultrasonic dispersion at least six times to remove any residual reagents.

(iii) Fabrication of SiO₂ photonic crystal template. SiO₂ photonic crystal templates were fabricated using a vertical deposition method described elsewhere [4]. ITO glass substrates (25 mm×10 mm) were cleaned with acetone and ethanol and then rinsed thoroughly with double-distilled water. The glass substrates were placed vertically in a beaker containing a dilute ethanol suspension of the SiO₂ colloidal spheres. The beaker was kept in a chamber at 30°C for about 2 days. After evaporation of the solvent, films of SiO₂ photonic crystals were obtained.

(iv) Growth of SiO₂-ZnO composite photonic crystal films. Electrodeposition and calcination were used to fabricate SiO₂-ZnO composite photonic crystals. The electrodeposition experiments were carried out with a standard three-electrode system with Pt as the counter electrode, a saturated calomel electrode as the reference electrode, and the ITO substrates with silica photonic crystal films as the working electrodes. The electrolyte used was 0.1 M

Zn(Ac)₂. The working potential was set at −1.0 V, and a deposition time of 5, 10, or 20 min was used. After electrodeposition, calcination in the air atmosphere at 500°C for 2 h was required to synthesize the SiO₂-ZnO composite photonic crystals.

2 Results and discussion

2.1 Morphology of the silica template

Figure 1(a) shows the top view of the SiO₂ photonic crystal template fabricated by vertical deposition. It shows that SiO₂ colloidal spheres with a diameter of about 250 nm are close packed, evidenced by a random sphere touching the other six ones in one layer. Although it is difficult to distinguish between the face-center-cubic (fcc) and hexagonal close-packed (hcp) structures, theoretical calculations have indicated that the fcc structure is stabilized slightly [15]. Each layer orients with its (111) axis parallel to the substrate in FCC packing, although there are some intrinsic defects such as line and dot defects. Figure 1(b) shows the side view of the SiO₂ photonic crystal template. The thickness of the SiO₂ photonic crystal template is about 11 μm.

2.2 The morphology of SiO₂-ZnO composite photonic crystal films

Figure 2(a) and (b) are scanning electron micrographs (SEM) of fractured parts of the SiO₂-ZnO composite photonic crystals fabricated at −1.0 V in 5 minutes. It is clear that the ZnO particles randomly adhere to the surfaces of the SiO₂ spheres and the grain size is not uniform.

Figure 3(a) and (b) show top views of the SiO₂-ZnO composite photonic crystals fabricated at −1.0 V in 10 minutes. The images show that the ZnO particles have adhered evenly to the surfaces of the SiO₂ spheres, although some irregular linear-shaped ZnO materials are observed in the interstitial space of the SiO₂ spheres.

Figure 4(a), (b) and (c) show top and side views of the SiO₂-ZnO composite photonic crystals fabricated at −1.0 V in 20 min. The interstitial space of the SiO₂ photonic crystal template is completely filled with ZnO.

Figure 1 SEM images of the as-deposited silica photonic crystal film. (a) Top view and (b) side view.

Figure 2 SEM images of a SiO₂-ZnO composite photonic crystal film prepared by electrodeposition for 5 min.

Figure 3 SEM images of a SiO₂-ZnO composite photonic crystal film prepared by electrodeposition for 10 min.

Figure 4 SEM images of a SiO₂-ZnO composite photonic crystal film prepared by electrodeposition for 20 min.

From the above observations the following assertion can be made: during the process of electrodeposition, the charge of the Zn ion is positive. Thus, a negative voltage is applied to the working electrode to push Zn ions towards the SiO₂ photonic crystal template. Electrons are transported from the ITO-glass substrate through the interstitial space of the SiO₂ photonic crystal template, where they combine with the Zn ions. The Zn particles grew randomly on the surfaces

of the SiO₂ spheres when the deposition time was short. As the deposition time lengthened, the Zn particles began to grow evenly on the surfaces of the SiO₂ spheres so that the interstitial space of the SiO₂ photonic crystal template was filled with Zn particles. The SiO₂-ZnO composite photonic crystals were fabricated during the calcination process. The diameter of Zn ions is much smaller than that of the Zn nanoparticles, and the metal Zn grew randomly on the sur-

faces of the SiO₂ spheres. This shows that electrodeposition does not have the disadvantage of blocking the nanochannels near the SiO₂ photonic crystal surface like electrophoretic deposition [12].

2.3 Optical characterization

The stop band position of the opal structure can be described with Bragg's law:

$$\lambda_{\max} = 2d_{111}\sqrt{n_{\text{avg}}^2 - \sin^2 \theta}, \quad (3)$$

$$n_{\text{avg}} = \sqrt{n_c^2 f + n_v^2 (1 - f)}, \quad (4)$$

where d_{111} is the distance between the neighboring (111) planes, n_{avg} is the effective refractive index of the structure, n_c is the refractive index of the colloidal sphere, n_v is the refractive index of the void or fillings, f is the filling factor (in this work, $f=74\%$), and θ is the impinging angle between the incident light and the normal of the substrate (in this work, $\theta=0$). Here, for the FCC structure, d_{111} is equal to $\sqrt{3}/3 D$ where D is the diameter of the colloidal sphere.

Figure 5 shows the normal reflectance spectra of the SiO₂ photonic crystal template and the SiO₂-ZnO composite photonic crystal films prepared with different deposition times. $\Delta\lambda$ is the full width at half maximum and λ is the position of the stop band. The height of the reflectance peak ($h(\%)$) and the fractional band width ($\Delta\lambda/\lambda$) of these samples were compared to assess their quality: a low reflectance peak and a peak broadening effect can be attributed to disorder within the structure [16,17]. A higher reflectance peak and a lower value for the fractional band width correspond to a better quality photonic crystal film because it indicates that ZnO materials have grown more evenly on the

SiO₂ spheres and in the interstitial space of the SiO₂ photonic crystal template.

From the optical properties shown in Table 1 the following observations can be made: (1) all of the fabricated photonic crystals exhibit a photonic band gap in the normal direction, and (2) the position of the stop band changes systematically with the deposition time according to Bragg's law. The measured stop bands (the positions of the reflectance peaks) of the SiO₂ photonic crystal template and the SiO₂-ZnO composite photonic crystals films prepared in 20 minutes agree very well with the calculated results according to Bragg's law. The height of the reflectance peak is low and the fractional bandwidth is large for the SiO₂-ZnO composite photonic crystals film prepared with a short deposition time. This is because during short deposition times the ZnO particles adhere randomly on the surfaces of the SiO₂ spheres, producing a disordered structure. As the deposition time increased, the height of the reflectance peak become higher and the fractional bandwidth become smaller, because interstitial spaces of the SiO₂ photonic crystal template are filled with ZnO, resulting in a more ordered structure. These results correspond closely with those from SEM.

3 Conclusions

In this study, SiO₂-ZnO composite photonic crystals were successfully prepared by electrodeposition and calcination. The influence of deposition time on the morphology and optical properties of the SiO₂-ZnO composite photonic crystals were investigated. It was found that ZnO particles adhere randomly to the surfaces of the SiO₂ spheres and the optical properties of the SiO₂-ZnO composite photonic crystals are poor when the deposition time is short. As the deposition time was increased, the ZnO coated the silica spheres evenly so that the interstitial spaces of the SiO₂ photonic crystal template were filled, resulting in SiO₂-ZnO composite photonic crystals with good optical properties. It was found that electrodeposition did not block the nanochannels near the surface like other deposition methods.

Table 1 Optical characterization of the silica template and SiO₂-ZnO composite photonic crystals fabricated by electrodeposition for different periods of time^{a)}

Optical properties	λ_c (nm)	λ_m (nm)	$\Delta\lambda/\lambda(\%)$	$h(\%)$
Silica template	556	560	13.5	23.7
SiO ₂ -ZnO film fabricated in 5 min	—	593	17.1	17.3
SiO ₂ -ZnO film fabricated in 10 min	—	624	11.1	21.1
SiO ₂ -ZnO film fabricated in 20 min	676	660	9.5	32.3

a) λ_c is the calculated stop band, λ_m is the measured stop band, $\Delta\lambda/\lambda(\%)$ is the measured fractional bandwidth value, and $h(\%)$ is the height of the reflectance peak.

Figure 5 Reflectance spectra of (a) the SiO₂ photonic crystal template and SiO₂-ZnO composite photonic crystals fabricated by electrodeposition for (b) 5 min, (c) 10 min, and (d) 20 min.

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