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Precise Fabrication of Point Defects in Self-Assembled Three-Dimensional Macroporous Photonic Crystals

Rongguo Xie

Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba 305-0047, Japan, and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

Takashi Sekiguchi*

Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba 305-0047, Japan

Dongsheng Li and Deren Yang

State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

Minhua Jiang

State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China, and State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China

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We demonstrate a new and simple method of precisely fabricating defects in three-dimensional (3D) CdS macroporous photonic crystals (PCs) with a variable pressure scanning electron microscope. Well-defined point defects, not only vacancies but also an impurity (a reduced-size sphere), were directly fabricated by electron-beam irradiation under a gas atmosphere. This provides a convenient and straightforward method of introducing various designed defects into 3D PCs for photonic-band-gap-based applications.

Three-dimensional (3D) photonic crystals (PCs) have attracted much attention in the past decade from both fundamental and practical viewpoints.[1,2] Various applications have been proposed using 3D PCs, such as low-loss waveguides, optical cavities, and zero-threshold lasers.[3,4] To achieve such applications, it requires exact placement of well-defined defects in the PCs. Self-assembly of colloidal spheres provides a simple and inexpensive approach to the fabrication of 3D PCs with high structural and optical quality.[5−13] However, well-defined point or line defects in the PC cannot be obtained through self-assembly alone. Defects engineering is therefore an important issue for producing photonic-band-gap (PBG)-based devices from the self-assembled 3D PCs. Many efforts have been made to incorporate linear defects in the self-assembled 3D PCs.[14−19] Point defects have also been randomly introduced by doping a self-assembled PC with impurity spheres of different sizes or different dielectric strengths.[20,21] However, the introduction of sub-micrometer point defects exactly placed in the self-assembled 3D PCs has proven quite difficult. Electron-beam (e-beam) writing has been used to produce deterministic microcavities in a PC made of poly(methyl methacrylate) (PMMA) spheres.[22] However, this technique is limited to the e-beam-sensitive polymers, which cannot be implemented to the high-refractive-index semiconductor materials. Furthermore, it is problematic to produce 3D PCs with a complete PBG using such polymer colloidal crystal. While the focused ion beam (FIB) technique is powerful for producing point defects, it requires an additional e-beam source for the observation of the specimens.

Here, we develop a new and versatile method of directly fabricating sub-micrometer point defects in macroporous CdS PCs with a variable pressure scanning electron microscope (VP-SEM). By using e-beam irradiation in a gas atmosphere, we can not only directly remove a sphere to fabricate a vacancy but also reduce the size of the sphere in a controllable manner to introduce an impurity in the macroporous PCs.

The CdS macoroporous PCs were fabricated via self-assembly of the CdS hollow spheres into face-centered-cubic structures. It includes the following steps. First, silica spheres were synthesized using a modified Stöber−Fink−Bohn method.[23] The silica/CdS core−shell structures were then fabricated by homogeneously depositing CdS nanoparticles on the surface of the silica spheres using a controlled deposition approach.[24] The detailed synthesis information is described elsewhere (see the Supporting Information). After the inner silica cores had been removed with a 1% HF aqueous solution, CdS hollow spheres were obtained. The hollow spheres were washed with water and ethanol by repeated centrifugation/dispersion cycles five times. Then, the hollow spheres were dispersed in ethanol for self-assembly. A 1 vol % concentration suspension of CdS hollow spheres was employed. After slowly drying the ethanol suspen-

* Corresponding author. E-mail: Sekiguchi.Takashi@nims.go.jp.

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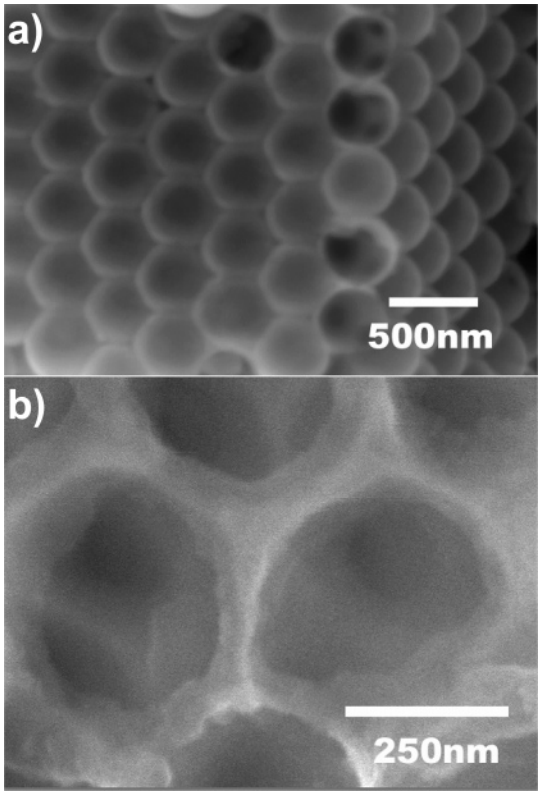

Figure 1. (a) SEM image of a CdS macroporous PC made of sphere A. (b) Cross-sectional SEM image (high magnification).

sion at room temperature over 5 days, macroporous PCs made of the CdS ($n = 2.4-2.5$) hollow spheres were obtained. By controlling the diameters of the silica spheres and the deposition time, hollow spheres with different diameters (200−900 nm) and different shell thicknesses (10−60 nm) were fabricated. In this work, two series of CdS hollow spheres were used. Sphere A had a diameter of ∼460 nm and a shell thickness of ∼25 nm, and sphere B had a larger diameter of ∼840 nm and a thicker shell of ∼60 nm.

A VP-SEM equipped with a field emission gun (Hitachi S-4300E/N) was used to fabricate the defects. In low-vacuum mode, gases, such as N_2 (>99.999%), O_2 (>99.99%), or H_2O (water vapor), were introduced into the specimen chamber. The VP-SEM was operated at 10−30 kV under gas pressures ranging from 10 to 100 Pa. The beam current was in the range ∼0.8−2.0 nA. An environmental secondary electron detector (ESED) was used to acquire the SEM images.

Figure 1a shows a SEM image of a macroporous PC made of the CdS hollow spheres, indicating good crystal quality. We can also see that the interstitial spaces between the assembled hollow spheres have been shrunk due to surface tension. This makes the PC stable. Figure 1b shows a high-magnification SEM image of a cross section of the PC, demonstrating an inverse-opal-like structure.

During the observation of the CdS macroporous PCs in the VP-SEM, we found that a stationary e-beam irradiation in the gas atmosphere had eliminated the CdS, thus resulting in a hole on a CdS hollow sphere. The size of the hole was usually less than 200 nm after 5 min of irradiation. Applying this phenomenon, we had precisely removed the CdS hollow spheres in the PC by successively irradiating the different regions to fabricate a vacancy. Figure 2 illustrates how the vacancies were directly fabricated in a PC. The as-cleaved PC made of sphere A was highly ordered with few intrinsic defects, as shown in Figure 2a. An e-beam of 30 keV was irradiated in spot mode on a

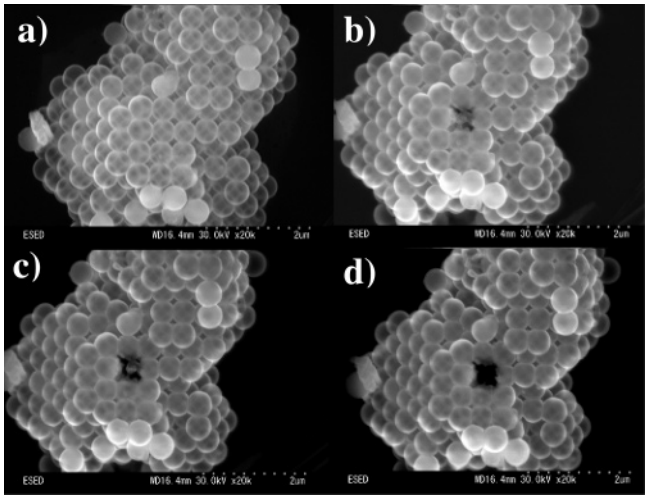

Figure 2. SEM images demonstrating vacancy fabrication. The e-beam was 30 keV in spot mode under a N_2 atmosphere of 20 Pa: (a) a cleaved PC made of sphere A before irradiation; (b) after 20 min of irradiation; (c) after 50 min of irradiation; (d) after 80 min of irradiation.

selected sphere under a N_2 atmosphere of 20 Pa. The duration of each irradiation exposure was 5 min. After successive irradiations at different spots on the CdS hollow sphere for 20 min, the hollow sphere was eliminated; thus, a single vacancy was fabricated, as shown in Figure 2b. From the figure, it can be seen that few residual CdS particles of the processed sphere were distributed on the top surface of the deeper layer. Under further e-beam irradiations, most of the CdS at the irradiated spot was eliminated, whereas little residual CdS was redistributed to the surrounding of the irradiated spot. Figure 2c shows the SEM image of the PC after irradiation for 50 min. It can be observed that there were still some CdS shells remaining at the center of the processed region. By carefully moving the e-beam on different spots in this region for irradiation, the CdS was completely eliminated. After irradiation for 80 min, the vacancies in the PC were fabricated, as shown in Figure 2d. Such vacancies were expected to act as cavities where the light was trapped through this channel.

Aside from fabricating vacancies, this technique also allows us to reduce the size of the CdS hollow sphere to fabricate an impurity in the PC in a controllable manner. In the normal scan mode (square mode), the CdS hollow spheres are generally stable and cannot be removed by e-beam irradiation even in a gas atmosphere. However, after a long period of irradiation, the irradiated hollow spheres shrink. Figure 3 shows how a single impurity (a reduced-size sphere) was fabricated in the PC. The VP-SEM was operated at an accelerating voltage of 10 kV under a N_2 atmosphere of 30 Pa. Figure 3a shows the starting PC made of sphere B. The e-beam was first irradiated on the hollow sphere in spot mode (Figure 3b) to open a hole. Five minutes of irradiation created a hole about 60 nm in diameter (Figure 3c). Afterward, the e-beam was irradiated beside the hole for 5 min to enlarge it (Figure 3d). The e-beam was then changed to square mode (Figure 3e) and irradiated at different regions around the hole. After 40 min, the sphere shrank significantly and the size of the hole was reduced (Figure 3f). Last, the e-beam was moved back to the hole and irradiated in square mode to seal it (Figure 3g). After 20 min, the hole was completely sealed (Figure 3h). As a result, the diameter of the CdS hollow sphere was reduced by ∼25% from 455 to 345 nm. With this technique, it is possible to tune the defect size, which results in the fabrication of defect states over a wide range

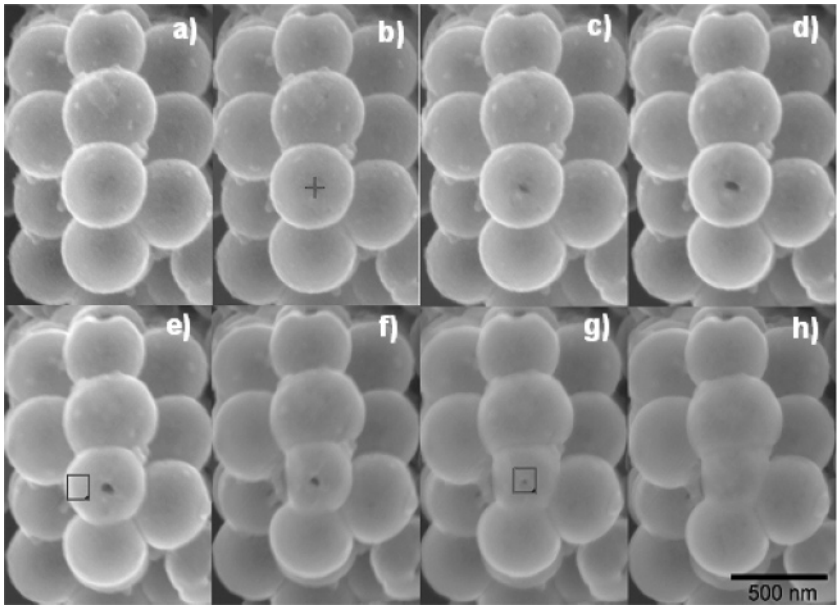

Figure 3. SEM images of the fabrication of an impurity (reduced-size hollow sphere). The e-beam was 10 keV under a N_2 atmosphere of 20 Pa: (a) initial PC made of sphere A; (b) irradiated point in spot mode; (c) after 5 min of irradiation; (d) after 10 min of irradiation; (e) irradiated region in square mode; (f) after irradiation at different regions around the hole over 40 min; (g) irradiated region on the hole; (h) after a further 20 min of irradiation.

of the PBG. Such defects are expected to act as microcavities to construct low-threshold lasers and light-emitting diodes.

Although this technique is powerful to fabricate not only vacancies but also a single impurity precisely in the PCs, it is not clear why e-beam irradiation in a gas atmosphere can either remove or shrink CdS hollow spheres. To clarify this mechanism, we varied the process conditions, such as beam voltage, current, and gas conditions. To investigate this effect reliably, sphere B was used. In high-vacuum mode ($<10^{-3}$ Pa), no removal of CdS was observed even under the highest-intensity (30 keV, ~2.0 nA) e-beam irradiation, suggesting the gas in the specimen chamber plays an important role for removal. In low-vacuum mode, we studied the effect of gas pressure (10−100 Pa) on removal efficiency. The SEM image in Figure 4a shows holes opened under different N_2 pressures. The inset shows those under a H_2O atmosphere. Each sphere was irradiated with an e-beam of 20 kV for 5 min in spot mode. The gas pressures are indicated in the image. To clarify the dependence of removal efficiency on gas pressure, the equivalent diameters of holes measured from Figure 4a have been illustrated in Figure 4b. We can see that, under both N_2 and H_2O atmospheres from 10 to 100 Pa, the removal efficiencies were highest at 10 Pa and generally decreased with increasing gas pressures. When the pressure was increased to above 80 Pa, little of the CdS was observed to have been removed.

On the basis of the above experimental results, we propose that CdS hollow spheres are mainly removed by gaseous ion sputtering driven by a large electric field set up by charging. When a specimen is irradiated by a high-energy (10−30 keV) e-beam, the surface is generally negatively charged. In a VP-SEM, the positive gaseous ions formed by collisions between electrons and gaseous molecules can hit the surface of the specimen to reduce surface charging.[25,26] These gaseous ions are mainly directed by the electric field set up by surface charging. In the normal square mode, as the e-beam moves frequently from one spot to the next so that the surface charge density becomes low, it is difficult for the gaseous ions to approach the threshold for sputtering. However, e-beam irradiation and ion collision lead to shrinking CdS hollow spheres. In

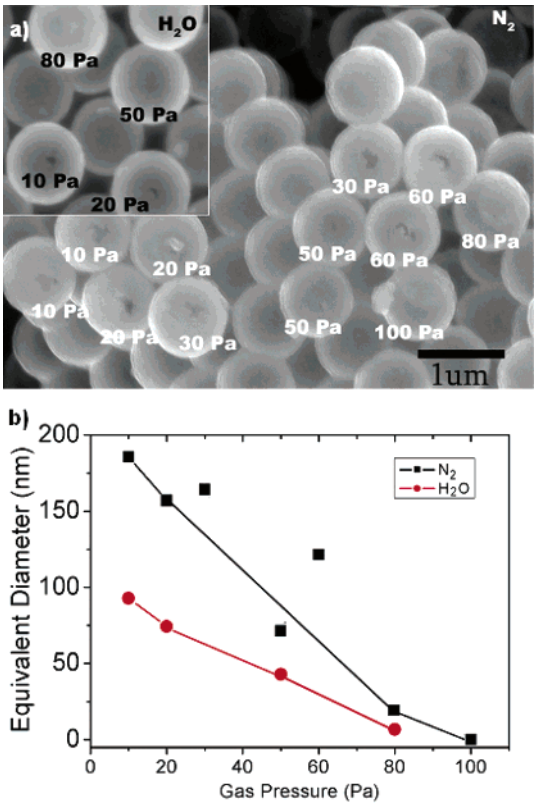

Figure 4. (a) SEM images of holes on sphere B opened by e-beam irradiation under a N_2 atmosphere of different pressures. The inset shows those under a H_2O atmosphere. The duration of each irradiation was 5 min. (b) Dependence of the equivalent diameters of opened holes on gas pressure.

spot mode, the specimen is intensively irradiated by the stationary e-beam. Under lower pressures (especially under 10 Pa), the specimen charges up more quickly than it discharges; as a result, the electric field in the irradiated region builds up until it is very large. The gaseous ions collide at the target at a high rate, and ion sputtering takes place, thus causing the target to be removed. However, under relatively higher gas pressures,

the surface potential may frequently stabilize at zero, making it difficult for gaseous ions to approach the threshold. In addition, the scattering of the primary e-beam by gas molecules becomes more serious with increasing gas pressure. Therefore, the removal efficiencies decrease with increasing gas pressure.

Compared with the FIB technology, our technique takes advantage of the VP-SEM with its capabilities for both in situ processing and observation at high resolution. Thus, it eliminates the need to use an additional e-beam source for imaging. Furthermore, the use of gas ions for the sputtering allows us to avoid the contamination from the ion source during the process. Although this technique is still limited to the upper layers of the PCs, it might be extended to fabricate the point defects in the interior of the PCs by subsequent growth of a secondary PC on the surface in a way similar to that for fabricating line defects in the interior of the PCs.[17−19] We have also applied this method for the cutting and bending carbon nanotubes,[27] extending its application to the precise processing of other nanostructures.

In conclusion, we have demonstrated a new straightforward yet versatile method of precisely fabricating well-defined point defects in self-assembled CdS macroporous PCs. Two kinds of point defects were site-selectively fabricated by e-beam irradiation under the gas atmosphere in a controllable manner, which will enable more complex structures in PCs to be fabricated. Judging from the various advantages, including the versatility of the fabrication process and the convenient in situ control of the e-beam for both observation and defect fabrication, we believe that our method holds great promise for the development of 3D PBG-based devices, such as low-threshold lasers and optical microcavities.

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Supporting Information Available: Detailed information on the preparation of monodisperse silica/CdS core−shell spheres. This material is available free of charge via the Internet at http://pubs.acs.org.

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