Vol 17 No 4, April 2008
1674-1056/2008/17(04)/1298-07

Chinese Physics B

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Observations of defect propagation in [100]-oriented opal-type photonic crystals

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(Received 6 February 2007; revised manuscript received 29 October 2007)

Charged colloidal suspensions have been used as experimental models for the study of crystal nucleation. Here we propose that the technique of template-assisted colloidal self-assembly can be used to visualize the effects of defect propagation in atomic crystal films produced using epitaxial growth. Templates with periodic line defects were used to grow [100]-oriented three-dimensional photonic crystals by means of the template-assisted colloidal self-assembly method, aided by capillary and gravitational forces. The defect propagation in the [100]-oriented photonic crystal was observed using scanning electron microscopy, both at the surface of the crystal and on cleaved facets. This method is useful in the understanding of defect propagation in the growth of colloidal films on templates - and the same approach may also prove useful for the understanding of atomic crystal growth on substrates with defects. Additionally, the deliberate incorporation of line defects may prove valuable as a way of introducing waveguide channels into three-dimensional photonic crystals.

Keywords: photonic crystal, colloidal crystal, self-assembly
PACC: 4270Q, 8116D, 8270D

1. Introduction

The structures of liquids, crystals and glasses have been studied extensively using the hard-sphere model. Mono-disperse colloidal suspension solutions are ideal mesoscopic models for the study of the fluid-to-crystalline state transition.[1−4] Many experiments have been performed to visualize the nucleation of colloidal crystals[5−7] in order to understand the nucleation mechanisms of atomic crystals. The usual orientation of crystallization for opal-type colloidal crystals is arranged with the face-centred cubic (fcc) [111] direction perpendicular to the substrate. However, functional crystal films have attracted more and more interest recently because of their possible applications in sensors and optoelectronic devices.[8,9] Epitaxial atomic crystal films are routinely grown on the (100) plane, for example in materials such as Si and SiGe and GaAs. In order to achieve epitaxial growth, a lattice matched template (or substrate) is necessary for obtaining a [100]oriented crystal film. Even though x-ray diffraction analysis and transmission electron microscopy (TEM) are extensively used to analyse the quality of the films,[10,11] the visualization of defect formation is still a challenge. In this paper, a template-assisted self-assembly process is proposed to visualize defect structures. By deliberately introducing defects into the template to produce [100]-oriented fcc and face-centred tetragonal (fct) opal,[12] the propagation of defects through the structures has been observed via scanning electron microscopy (SEM). The results obtained could be useful in gaining a general understanding of the nature of defect propagation in crystals.

Colloidal crystals, which can be considered as a specific type of three-dimensional (3D) photonic crystal (PhC),[13] are the basis for the present work. There is a substantial body of literature concerned with the fabrication of high quality colloidal crystals.[14−31] Mono-disperse spheres can be deposited and dried on a substrate, forming a face-centred cubic lattice structure, using a variety of methods.[14−20] The surface of the resulting 3D (i.e. three-dimensionally periodic) PhC is usually oriented in the [111] direction. However, stacking faults are unavoidable in this type of crystal. To overcome this situation, the template-assisted self-assembly method was proposed.[20] Growth on a [100]-oriented template or substrate does not allow hexagonally close packed (hcp) structures.[20−25] However, we have recently

shown that, in general, a tetragonally distorted lattice is necessary for good quality growth of 3D PhC structures, and we have succeeded in the preparation of [100]-oriented 3D PhC films via a template-assisted colloidal self-assembly method, with the aid of capillary and gravitational forces. Moreover, our approach has demonstrated that the appearance of cracks may be eliminated[12] and therefore that large-area near-perfect 3D PhC films may be synthesized. However, because of the difference of the sphere sizes, defects may occur that affect the quality of the [100]-oriented 3D PhC films produced. This paper describes how the propagation of defects can be studied through their deliberate introduction. Crystal defects are initiated from periodic line defects in the template on which the crystal was grown. This deliberate initiation helps in the understanding of the propagation of defects and controlling of the quality of the crystal, and may thus simultaneously introduce waveguide-like structures into the crystal.

2. Fabrication

A single-crystal silicon substrate was cleaned in the following procedure. First it was cleaned in acetone with ultrasonic treatment for 5 min. Subsequently, the substrate was cleaned in methanol solvent with ultrasonic treatment for 5 min - and then it was dipped in ethanol with ultrasonic treatment for another 5 min. After that, the substrate was dried by using a nitrogen gas gun, and put in H_2SO_4:H_2O_2 solution for 10 min. Then the substrate was finally rinsed with deionized water, and blow-dried with nitrogen gas. The dried substrate was placed into an oven at 180°C and kept for at least 1 h in order to remove the water on the surface. A layer of hydrogen silsesquioxane (HSQ) (Dow Corning Fox 14) resist with a thickness of around 160 nm was spin-coated onto the substrate. Then the template pattern was defined by using electron beam lithography. The resist was developed in a solution of tetra-methyl ammonium hydroxide (TMAH) and periodic pillars were formed in the HSQ layer. After that the processed substrates were heated in an oven at 400°C for 1 h in a nitrogen atmosphere, in order to ensure adhesion of the resist to the silicon wafer.[32] A 2D-periodic template with single-row, periodic line-defects is shown in Fig.1, where the lattice constant of the template is 312 nm, and the period of the line defects is specified as 12.792 μm. The periodicity of the line defect patterns is not of particular significance but helps in their identification.

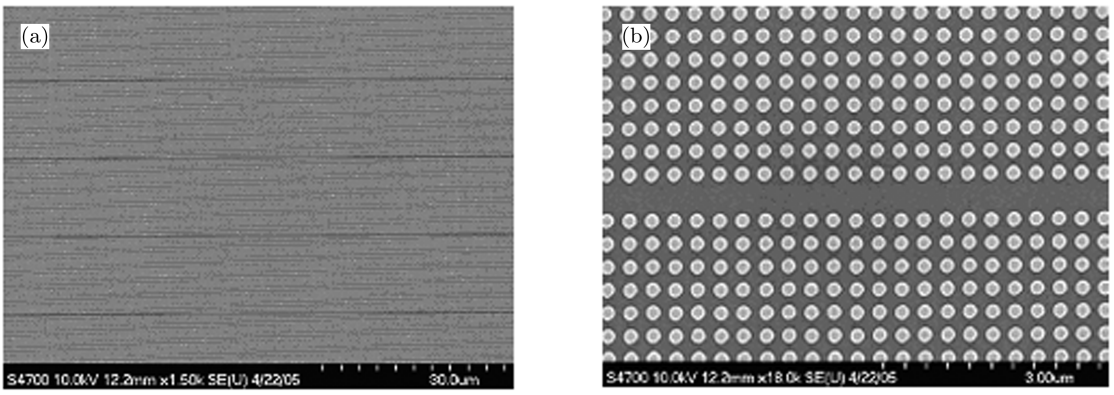


Fig.1. (a) Templates with periodic line defects, where the period of the line defects is 12.792 μm and the lattice constant of the template is 312 nm; (b) a magnified view of the area shown in (a).

Polystyrene spheres were purchased from the Duke Scientific Company. The diameter of the spheres in a dry state was 299 ± 4.1 nm. Template-assisted colloidal self-assembly with the aid of capillary and gravitational forces was employed to grow [100]-oriented 3D photonic crystals.[12] A setup is shown schematically in Fig.2. The templated substrate was set at an angle of 45 degrees to the horizontal plane throughout the crystal growth process. Growth temperature was set at 23.4°C, with an ambient relative humidity of 32%–34%. The diameter of the polystyrene spheres used was 299 ± 4.1 nm and the evaporation speed of

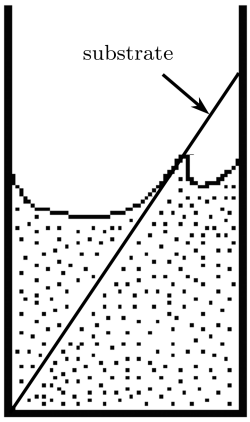


Fig.2. Schematic setup for the template-controlled growth of [100]-oriented 3D photonic crystals.

the solution was around 1 mm/day. A detailed description of the growth process is given in Ref.[12]. Since the template is a square periodic array of pillars, the crystal formed must be a face-centred cubic lattice structure when the diameter of the spheres is the same as the lattice constant of the template,[20] and the surface is [100]-oriented. If the diameter of the spheres is less than the lattice constant of the template, it will form a face-centred tetragonal lattice structure, but the surface is still correctly indexed as (100).[12] In this paper, because the diameter of the spheres is less than the lattice constant of the template, the crystal formed is a face-centred tetragonal one whose surface is (100).

3. Results and discussion

3.1. Growth of opal along the direction of defect line on the template

When the direction of the line defect is aligned along the growth direction of the crystal, i.e. the direction is parallel to the slope of the substrate, the typical patterns observed on the top surface of the [100]-oriented 3D photonic crystals are shown in Figs.3(a) and 3(b).

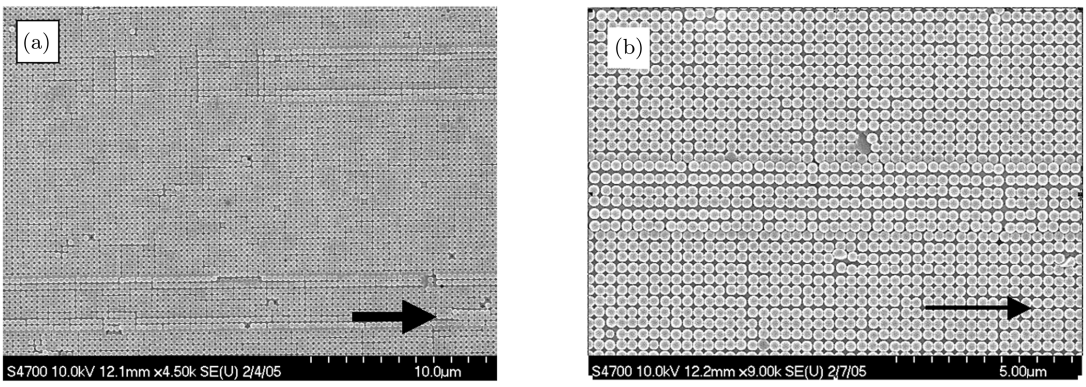


Fig.3. SEM images of [100]-oriented 3D photonic crystal grown on templates with periodic line defects oriented parallel to the growth direction:- the arrow indicates the growth direction of the crystal.

From Figs.3(a) and 3(b), it is clear that there are periodic defects composed of stripes of six to ten lines of spheres on the surface. Most of the defect areas appear well arranged along the growth direction. However, in the defect areas, the distance between two spheres at the surface in the direction orthogonal to that of the line defect is larger than the normal period of the template. At the interface between the defect area and the main crystal area, there is a half lattice-constant shift as compared with the normal [100] 3D photonic crystal. The period of the defects is the same as the period of the line defects on the template ($12.792\,\mu$m). Compared with the single-row line defects on the template, the defect on the top surface of the crystal is much wider, implying the formation of a distinct wedge-shaped stripe region of crystal. For this orientation the defects can appear intermittently along the whole line of missing pillars.

In order to study the propagation of the defect from the bottom layer to the top layer of the 3D PhC film, the crystal was cleaved along a surface orthogonal to the defect line. Figures 4(a) and 4(b) show SEM images of the cleaved facet of a [100]-oriented photonic crystal with periodic line defects. When the first deposited spheres meet the line defect defined before on the template, it is possible that two rows of spheres should be arranged partially into a single-row line defect. But Fig.4(a) shows that only one sphere appears in this area, thus leaving a substantial amount of space. As a result, the second layer of deposited spheres cannot be properly arranged, and the defect area extends progressively and diagonally, as the number of deposited layers increases. Counting from the surface, the width of the defect has expanded to nine lines of spheres after the deposition of seven layers. Because the spheres in the bottom layer of the crystal are not, in general, located exactly at the centre-line of the template line defect, the defect has an asymmetric shape. From Fig.4(a), it can be seen that there are two lines of spheres that are isolated from the others on the left hand side of the defect area while, on the right hand side, the defect area is separated by a line of spheres with a half lattice constant shift in position, as compared with the main crystal lattice. The defect can develop in different ways and form various patterns on the surface. Figure 4(b) shows the other typical pattern formed by the line defect. The profile of the defect looks like a V-shaped groove. If the spheres are arranged on the template simultaneously over the area under consideration, the crystal defect cannot extend outside of the single-row line defect defined by the template. This reveals that, for the growth of [100]-oriented crystal films, the spheres arrange themselves on the template layer-by-layer. This phenomenon indicates that the template-assisted growth of opal is similar to the method of molecular beam epitaxy for the growth of atomic and molecular crystal films. Observations of the growth of colloidal crystals with induced defects may therefore be useful to evaluate the effect of the substrate on the quality of the film, because it is easy to monitor in real-space. In some cases, if the spheres arrange themselves appropriately into the template defect area, defects may disappear, as observed at the surface of the film.

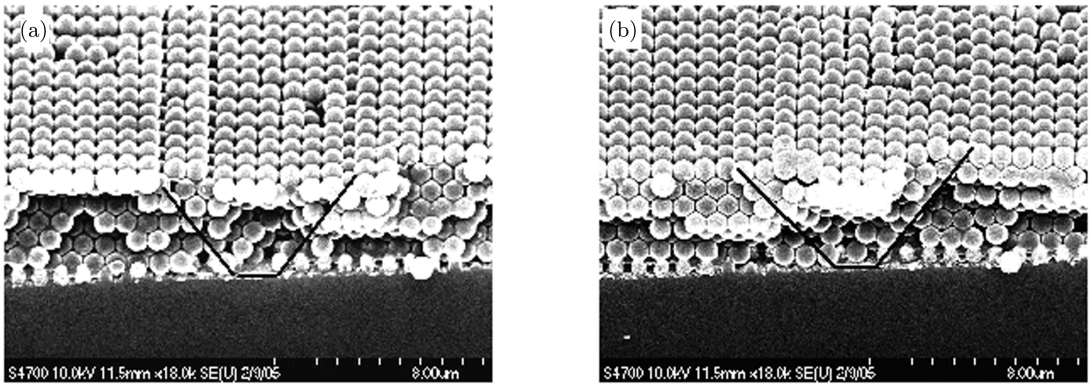


Fig.4. SEM micrographs of the cleaved facet of the [100]-oriented 3D photonic crystal grown on a template with periodic line defects whose direction is parallel to the growth direction. The V-shaped black lines indicate the profiles of the defect regions.

3.2. Growth of opal perpendicular to the direction of line defects on the template

To understand the effect of the direction of the line defects on the crystal structure, the crystal growth was arranged with periodic line defects perpendicular to the growth direction. The top surface of such crystals is shown in Fig.5. In most cases, the defect disappears, as shown in Fig.5(a). However, when the defect is initiated as shown in Fig.5(b), it is clear that, at the surface, the defect is wider than the defect formed in the template by single-row line defects whose direction is along the growth direction. Furthermore, the defect is not a [100]-oriented structure but a random and hexagonal structure. It is also found that the defect does not form with the orientation of the line defect defined on the template, but with an orientation parallel to the growth direction of the crystal.

This situation is very different from that for a crystal formed on a template with line defects parallel to the growth direction. We can give a rough explanation by using a simple geometric model. For a template with periodic line defects, if the direction of the line defect is perpendicular to the growth direction, as shown in Fig.6(a), there is a barrier that can prevent spheres changing their position, in which the spheres on the bottom layer can have a high probability of being arranged into the correct position for growth of a regular lattice, and as a result only a few defects are initiated. When the direction of the line defects is parallel to the growth direction, however, there is no barrier to hold the spheres in the correct positions, and more defects can be initiated, as shown in Fig.6(b). It is still not clear why the defects formed on the template, with line defects perpendicular to the growth direction, are in random orientations or show a hexagonally packed surface structure; whereas in the parallel case the [100] orientation is maintained, but with parallel dislocations along the crystal growth. Further experiments are required, in which an attempt should be made to observe the colloidal nucleation in the neighbourhood of a line defect in real time. For the present case, the spheres used in our experiment are rather small for conveniently observing by confocal optical microscopy.

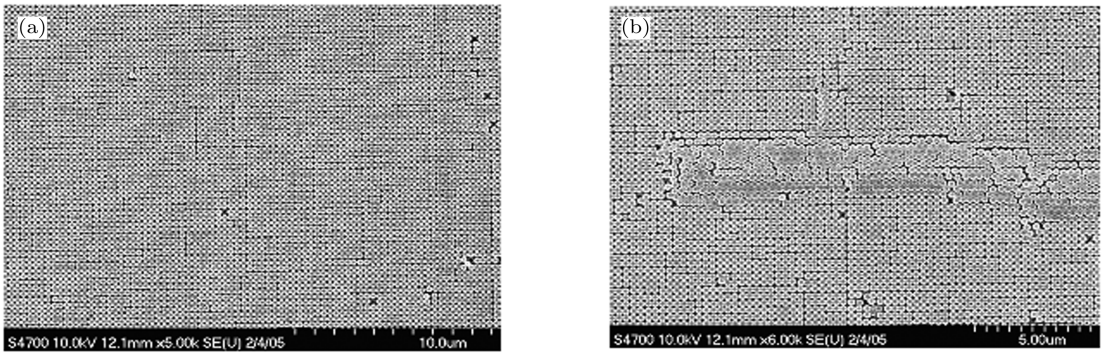


Fig.5. SEM images of the [100]-oriented 3D photonic crystal on a template with periodic-line defects whose direction is perpendicular to the crystal growth direction. The arrows indicate the growth direction. (a) No defect is initiated by the line defect of the template and, therefore, no defect can be found on the surface of the crystal. (b) A defect is initiated by the line defect on the template and then the defect propagates to the surface of the crystal.

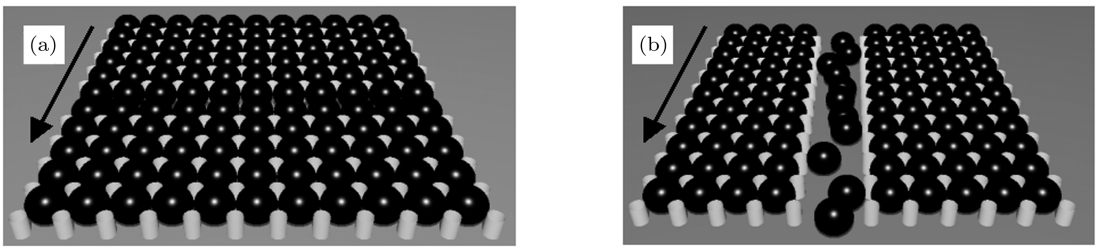


Fig.6. Schematic model of the spheres arranged into positions on the template with single-row periodic line defects, where an arrow indicates the growth direction. (a) The line defect is perpendicular to the growth direction. (b) The line defect is parallel to the growth direction.

Figure 7 shows the cleaved facet of a [100]-oriented 3D PhC on a template with periodic line defects whose direction is perpendicular to the growth direction. As is seen by examination of the surface, the line defect vanishes in most cases (Fig.7(a)). Sometimes, the crystal defect initiated from a single-row line defect in the template develops along the growth direction indicated by the arrow, which is perpendicular to the line defect. The defect area is not parallel to a [100] direction but is randomly oriented with irregular shapes and sometimes shows a hexagonal arrangement.

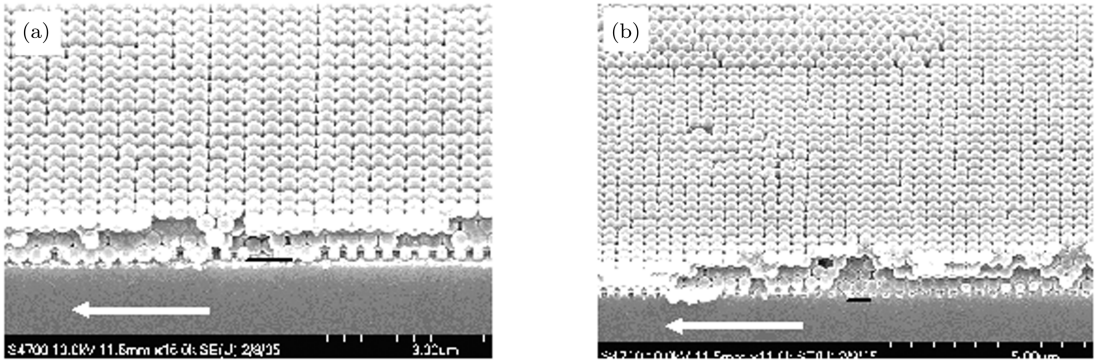


Fig.7. Cleaved facet of [100]-oriented 3D PhC grown on a template with periodic line defects oriented perpendicular to the crystal growth direction, where the arrows indicate the growth direction of the crystal. The black line indicates the position of the line defect on the template, as indicated by the missing pillars. (a) The spheres can be well-arranged, even though there is a line defect on the template, as indicated by the black line, and therefore no defect could be observed at the surface. (b) The defect was initiated by the line defect on the template and then propagates to the surface, forming a hexagonal structure.

3.3. Growth of opal on the template with point defects

The effects of various other defect structures in the template on the growth of the opal crystals were also studied, e.g. point, multipoint, and multi-line defects. The point defect in the template is very hard to locate and observe via a cleaved facet because it is very difficult to cleave a sample with a precision of one micrometre. It was found that relatively few defects are initiated by a single point defect in the template. When the multi-line defects on a template are composed of several missing pillar lines, the defects in the crystal have a greater possibility of initiation, as compared with the single-line defects in the template. Furthermore, most of the defects in the crystal initiated by multi-line defects of the template are in [111] or a random orientation, whether the direction of the multi-line defect of the template is parallel or perpendicular to the growth direction of the crystal.

4. Conclusions

We have demonstrated that the technique of template-assisted colloidal self-assembly can be used to visualize the effects of defects defined on patterned substrates and their propagation through the growing crystal to its surface. The effect of the line defects on the template on the growth of [100]-oriented 3D photonic crystal has been studied by observing the surface and cleaved facets of the crystals grown on templates with periodic single-row line defects. It was found that, when the direction of the line defects is parallel to the growth direction of the crystal, the defects initiated in the crystal always developed along the growth direction of the crystal. The defect initiated in the crystal propagates to its top surface and usually forms a wedge or V-shaped dislocation in the crystal. When the direction of the periodic line defects in the template is parallel to the growth direction, there are more defects initiated than typically observed for crystals grown on templates with single-row periodic line defects whose direction is perpendicular to the growth direction. We have proposed a simple geometrical model to explain this behaviour. These results are important for the deliberate introduction of defects or, conversely, for the reduction of defects produced in [100]-oriented 3D photonic crystals. This study could also be valuable in the evaluation of the effects of the substrate surface orientation on the growth of [100]-oriented crystal films via other epitaxial methods, e.g. atomic scale crystals.

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