# Semicrystalline woodpile photonic crystals without complicated alignment via soft lithography

Jae-Hwang Lee, Ping Kuang, Wai Leung, Yong-Sung Kim, Joong-Mok Park, Henry Kang, Kristen Constant, and Kai-Ming Ho

Citation: Applied Physics Letters **96**, 193303 (2010); doi: 10.1063/1.3425756
View online: http://dx.doi.org/10.1063/1.3425756
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/96/19?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **96**, 193303 (2010)

# Semicrystalline woodpile photonic crystals without complicated alignment via soft lithography

Jae-Hwang Lee,[1,a)] Ping Kuang,[2] Wai Leung,[3] Yong-Sung Kim,[3] Joong-Mok Park,[3] Henry Kang,[2] Kristen Constant,[2] and Kai-Ming Ho[1,b)]
[1]*Department of Physics and Astronomy, Ames Laboratory–U.S. D.O.E., Iowa State University, Ames, Iowa 50011, USA*
[2]*Department of Materials Science and Engineering, Ames Laboratory–U.S. D.O.E., Iowa State University, Ames, Iowa 50011, USA*
[3]*Ames Laboratory–U.S. D.O.E., Ames, Iowa 50011, USA*

(Received 31 August 2009; accepted 8 February 2010; published online 13 May 2010)

We report the fabrication and characterization of woodpile photonic crystals with up to 12 layers through titania nanoparticle infiltration of a polymer template made by soft lithography. Because the complicated alignment in the conventional layer-by-layer fabrication associated with diamondlike symmetry is replaced by a simple 90° alignment, the fabricated photonic crystal has semicrystalline phase. However, the crystal performs similarly to a perfectly aligned crystal for the light propagation integrated from the surface normal to 30° at the main photonic band gap. *© 2010 American Institute of Physics*. [doi:10.1063/1.3425756]

Three-dimensional (3D) photonic crystals (PCs) or photonic-band-gap (PBG) materials[1,2] are periodically patterned materials in which light's propagation and interaction with the material are significantly modified, in a certain range of frequencies, from those in a homogeneous medium. Because some PCs have a connected 3D network of voids, for example, the inverse opal structure,[3] the highly porous character presents opportunities for novel applications including, organic solar cells,[4–6] and photocatalysts for decomposing chemical waste.[7,8] Moreover, it is predicted that PCs could be applied to hydrogen production using photoelectrolysis.[9] Electrochemical reactions can be optimized by considering both the photonic performance and the proper 3D structure. Compared to the inverse opal structure, the layer-by-layer,[10] or woodpile structure should have advantages for photochemical applications because of its robust 3D PBG effect[11] and interconnected open-pores. There are reports of a number of fabrication methods for the woodpile PCs (Refs. 12–17) which attempt to overcome the high cost of conventional photolithographic fabrication,[17,18] however, they are still more costly and time consuming than the inverse opal methods mainly because of complicated interlayer alignment. Recently, we have proposed the possibility that a semicrystalline woodpile PCs, in which no a large size of crystallite exists, would function as a perfect PC.[19] Here, we demonstrate soft-lithographical fabrication of the semicrystalline woodpile PC, and confirm that the semicrystalline PCs indeed exhibit optical performance approaching that of a perfect crystal for incoming light with incident angle ranging from the surface normal to 30°. As the semicrystalline PC can create a photonic band structure for perpendicularly-incoming light as well as well-defined short pathways through the PC to a substrate for charge/mass transport, we believe the fabrication method and the semicrystalline PCs can be valuable in meeting the requirements for applying conventional photonics to photochemistry, which is inherently difficult for one-dimensional and two-dimensional PCs.

We have developed an alternative path to creating the woodpile PC using a soft-lithographically fabricated polymer template and titania slurry,[20] and here, we report an advanced fabrication technique for ceramic woodpile PCs via soft lithography to produce low-cost and high-quality PCs. In the schematic illustration in Fig. 1, the initial polymer template is fabricated by a soft-lithographic technique called two-polymer microtransfer molding[21] on a sacrificial-layer (AZ 6612KE, Clariant)-coated glass plate using alignment by diffracted moiré fringes.[22] As we stack the rods of each layer perpendicular to those of the layer below without considering lateral position, the fabricated template has semicrystalline structure including face-centered-tetragonal (FCT), tetragonal, and amorphouslike phases. Titania nanopowder (Nanotek® titanium dioxide, Nanophase Tech.) is mixed with distilled water to make a 20 wt % titania slurry, and sonicated in an ultrasonic bath for an hour to disperse the itania particles. By centrifuging for 5 min at 6000 rpm, agglomerated particles in the slurry were removed. The remaining slurry, ~15 wt % titania, is used for infiltration. After the

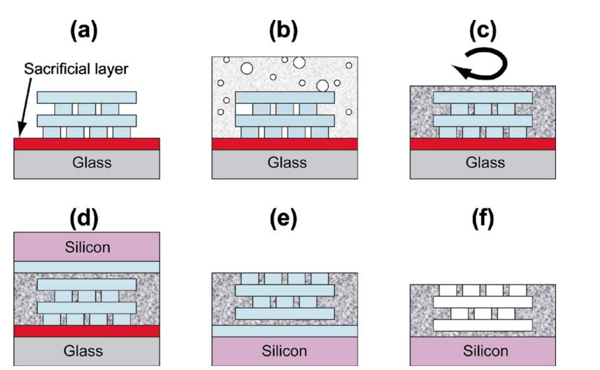


FIG. 1. (Color online) Schematic illustration of the fabrication procedure. (a) Template fabrication on a sacrificial-layer-coated glass plate. (b) Vacuum-assisted wetting of titania slurry. (c) Multiple spin-coating and drying. (d) Silicon wafer bonding with a photo-curable prepolymer. (e) Separation of glass plate by dissolving the sacrificial layer. (f) Firing.

[a)]Present address: Department of Materials Science and Engineering, MIT, Cambridge Massachusetts 02139, USA.
[b)]Electronic mail: kmh@cmpgroup.ameslab.gov.

 

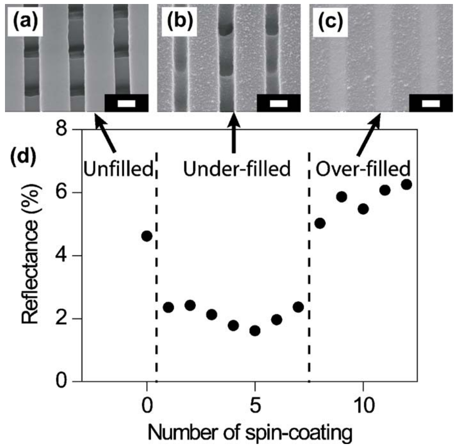


FIG. 2. (Color online) SEM micrographs of a template (a) unfilled, (b) under-filled, and (c) over-filled are shown to visualize the change on the morphology of the template as titania slurry is spun multiple times. The scale bar in the micrographs is 1 μm. (d) Reflectance of the template is monitored during the infiltration. The spectral reflectance is averaged in the range from 500–750 nm in wavelength.

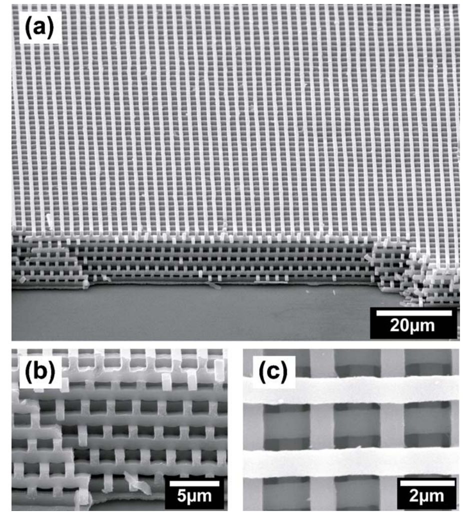


FIG. 3. (Color online) SEM micrographs of a 12-layer titania PC. Tilted SEM image of a cleaved edge at (a) lower and (b) higher magnifications; (c) top view.

titania slurry is applied to the template in a chamber at room temperature, the pressure is reduced until the water in the slurry starts to boil and then the system is allowed to recover to atmospheric pressure. Five cycles of depressurization are performed to remove air captured in the template. Excess slurry is subsequently removed by spinning. After the first infiltration, several consecutive spin-coatings of the slurry are performed in air until an even over-layer is formed. After drying of the infiltrated slurry, a $4\times4$ mm$^2$ piece of double-polished silicon wafer is bonded to the sample with a photocurable prepolymer (J91, Summers Optical). By UV exposure from the glass side, the prepolymer is fully cured while applying a pressure of 4 g/mm$^2$ to the silicon wafer. The sample is transferred to a silicon substrate by completely dissolving the sacrificial layer through submersion in isopropanol. Then the polymer template is removed by firing at 550 °C in air for one hour after a 1 °C/min ramp-up. Since an air gap between the titania structure and the silicon wafer remains, adhesion is achieved by applying diluted titanium diisopropoxide bis(2,4-pentadionate) (TDBP), 2 wt %. Excess TDBP is removed by blowing air.

For functionality, the removal of the over-layer is essential as it deteriorates the optical performance of a 3D PC by causing optical surface resonance.[23] Moreover, the uniform over-layer obviously isolates the internal space of a 3D PC from the outside, and results in poor electrochemical exchanges for some applications. We eliminate the effect of the thick titania over-layer without an additional etching processes by flipping the ceramic-infiltrated template over to expose the open structure previously in contact with the substrate.

Figure 2 shows how the slurry infiltration of a template is performed and controlled. Unlike gas-phase deposition, the solid content is carried by capillary action of the aqueous slurry into the structure's channels leaving the ceramic solid. Consequently, many voids remain inside and on the surface of the template as it dries as seen in Fig. 2(b). Through multiple spin-coatings, we can form an even layer of titania over the template without voids as seen in Fig. 2(c). The over-filling of the slurry is readily discernable by monitoring the reflectance of a template as seen in Fig. 2(d). The initial reflectance drops after the first spin-coating due to large scattering of light by many voids and sharply increases when a homogeneous over-layer is formed over the template. By this method we can consistently form an over-layer, approximately 0.5 μm thick. This simple and versatile infiltration method can be applied to other PC fabrication techniques using polymer templates.[12,13]

We fabricate PCs having two to twelve layers, where 4-, 8-, and 12-layer PCs are semicrystalline. A 12-layer PC is shown in Fig. 3 as an example of the results of infiltration. The PC has a total thickness of over 14 μm and $3.5\times3.5$ mm$^2$ in lateral dimensions. Each rectangular rod is 0.9 μm wide and 1.0 μm high and the center-to-center spacing is 2.5 μm, which corresponding to a filling ratio of 36%. A low-magnification scanning electron microscope (SEM) image (tilt angle of 60° to the surface normal) shows a well-defined large-area structure [Fig. 3(a)]. In a closer view [Fig. 3(b)], all 12 layers are clearly visible with an underlying layer, (which was once the over-layer). The quality of the resulting structure is very high and edges of each bar are as sharp as those in PCs made using conventional photolithography[17] due to the nonoptical nature of the fabrication. As previously stated, the structure is not aligned over the whole crystal but there are some partially aligned areas as seen in Fig. 3(c). There is no significant volume-shrinkage of the titania structure after firing.

The reflectance spectra of titania PCs on silicon wafers having different numbers of layers are measured by a Fourier-transform infrared spectrometer with a microscope (Bruker Hyperion 1000, 36× Schwarzschild objective mirror, numerical aperture=0.5, and liquid nitrogen cooled mercury-cadmium-telluride detector) with a sampling area of approximately $100\times100$ μm$^2$. In Fig. 4, the reflectance spectra are shown with the reflectance spectra of a bare silicon substrate and a bare titania plate from the same slurry. For a 2-layer PC [Fig. 4(a)], the reflectance spectrum shows no distinctive peak and follows that of silicon in the longer wavelength region ($\lambda>4$ μm). The reflectivity is slightly lower as the 2-layer PC scatters light rather than reflects coherently due to its incomplete half unit-cell. We also see an intrinsic absorption feature of titania in that region. The reflectance at wavelengths shorter than 4.5 μm drops consid-

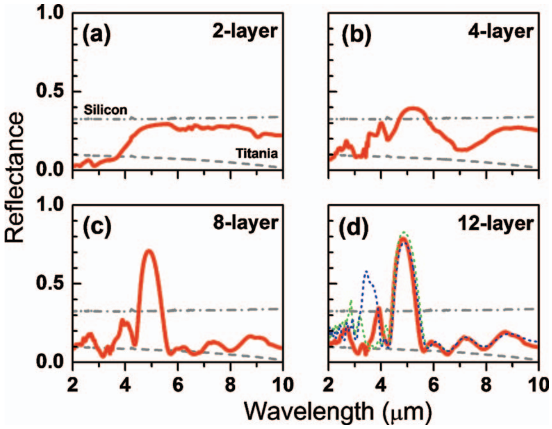


FIG. 4. (Color) Measured reflectance spectra of PCs having different numbers of layers are plotted (solid red). A bare silicon wafer (dashed dotted) and a bare titania plate (dashed) are also measured under the same conditions as references. (d) For comparison, calculated spectra for the 12-layer PC of FCT (green dotted) and tetragonal (blue dotted) structures are also coplotted.

erably because of diffraction from the PC structure and additional scattering from structural roughness. However, for 4-, 8-, and 12-layer PCs [Figs. 4(b)–4(d)], the reflectance at the main PBG around 5 $\mu$m consistently increases as a function of the number of layers over that of silicon in contrast to other peaks. For 4- and more layered PCs, the baseline of reflectance is closer to bare titania rather than to bare silicon because optical effect from the silicon substrate is shielded by the multiple layers. The peak reflectance of the 12-layer PC is about 0.8, which is almost tenfold higher than that of titania at the same wavelength. The theoretical reflectance spectra of FCT and tetragonal structures are calculated using the transfer-matrix-method[24,25] to evaluate the experimental results of unaligned structures. To consider the microporosity of the dried titania slurry, the refractive indices of crystalline anatase titania[26] are used in the calculations after reducing the indices 20%, where the reducing factor is determined by the measured reflectance of a titania slurry film prepared using similar procedures. Because the objective mirror of the microscope collects light within a range from 8° to 30°, the associated optical effect is accounted for by averaging reflectance spectra of different incident angles in that range. The calculated reflectance spectra in Fig. 4(d) are in very good agreement with the measured spectrum in the frequency region of the main band gap and at longer wavelengths. The discrepancy between the calculation and the experiment is obvious at shorter wavelengths because the optical effects from diffraction and alignment are considerable. It is worth emphasizing that the semicrystalline woodpile PC with only 90°-alignment could be very advantageous for applications utilizing its main PBG because its optical functionality is comparable to that of a perfectly aligned crystal.

The highest reflectance achievable is 0.8 (not unity). This saturation arises from two main sources, a low refractive index and absorption of the anatase-phase titania (n $\sim$2.0) in the mid-IR range.[26] However, the demonstrated reflectance is comparable or even higher than that of other woodpile PCs made of higher refractive index materials such as germanium[16] and $As_2S_3$ glass,[14] which implies that the structural fidelity of structure is also critical. Therefore, further improvement in reflectance is anticipated if higher refractive index materials were used.

In conclusion, in demonstrating a method of fabricating semicrystalline woodpile PCs by titania-slurry infiltration of polymer templates made by soft lithography, we show that high-quality woodpile PCs are achievable through nonoptical means without stringent interlayer alignment. The fabricated semicrystalline PCs have the main PBG at 5 $\mu$m and the reflectance approaches 0.8 for a 12-layer PC, almost the same values expected from the perfectly aligned PC for integrated incident angles up to 30°, in spite of non-negligible absorption in the material and the low refractive index of anatase phase titania. Because alignment is less important for the main PBG, we believe that this approach is quite promising and facilitates the use of woodpile PCs for more diverse applications including nonlinear-optical and photochemical devices with appropriate scaling.

This work is supported by the Director for Energy Research, Office of Basic Energy Sciences. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

[1]E. Yablonovitch, Phys. Rev. Lett. **58**, 2059 (1987).
[2]S. John, Phys. Rev. Lett. **58**, 2486 (1987).
[3]A. Imhof and D. J. Pine, Nature (London) **389**, 948 (1997).
[4]S. Nishimura, N. Abrams, B. A. Lewis, L. I. Halaoui, T. E. Mallouk, K. D. Benkstein, J. van de Lagemaat, and A. J. Frank, J. Am. Chem. Soc. **125**, 6306 (2003).
[5]A. Mihi, F. J. Lopez-Alcaraz, and H. Miguez, Appl. Phys. Lett. **88**, 193110 (2006).
[6]L. I. Halaoui, N. M. Abrams, and T. E. Mallouk, J. Phys. Chem. B **109**, 6334 (2005).
[7]Y. Z. Li, T. Kunitake, and S. Fujikawa, J. Phys. Chem. B **110**, 13000 (2006).
[8]J. I. L. Chen, G. von Freymann, S. Y. Choi, V. Kitaev, and G. A. Ozin, Adv. Mater. (Weinheim, Ger.) **18**, 1915 (2006).
[9]G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and G. A. Grimes, Nano Lett. **5**, 191 (2005).
[10]K.-M. Ho, C. T. Chan, C. M. Soukoulis, R. Biswas, and M. Sigalas, Solid State Commun. **89**, 413 (1994).
[11]A. Chutinan and S. Noda, J. Opt. Soc. Am. B **16**, 1398 (1999).
[12]N. Tétreault, G. v. Freymann, M. Deubel, M. Hermatschweiler, F. Pérez-Willard, S. John, M. Wegener, and G. A. Ozin, Adv. Mater. (Weinheim, Ger.) **18**, 457 (2006).
[13]G. M. Gratson, F. Garcia-Santamaria, V. Lousse, M. J. Xu, S. H. Fan, J. A. Lewis, and P. V. Braun, Adv. Mater. (Weinheim, Ger.) **18**, 461 (2006).
[14]S. Wong, M. Deubel, F. Perez-Willard, S. John, G. A. Ozin, M. Wegener, and G. von Freymann, Adv. Mater. (Weinheim, Ger.) **18**, 265 (2006).
[15]P. Yao, G. J. Schneider, D. W. Prather, E. D. Wetzel, and D. J. O'Brien, Opt. Express **13**, 2370 (2005).
[16]F. García-Santamaría, M. J. Xu, V. Lousse, S. H. Fan, P. V. Braun, and J. A. Lewis, Adv. Mater. (Weinheim, Ger.) **19**, 1567 (2007).
[17]S. Y. Lin, J. G. Fleming, D. L. Hetherington, B. K. Smith, R. Biswas, K. M. Ho, M. M. Sigalas, W. Zubrzycki, S. R. Kurtz, and J. Bur, Nature (London) **394**, 251 (1998).
[18]S. Noda, K. Tomoda, N. Yamamoto, and A. Chutinan, Science **289**, 604 (2000).
[19]J.-H. Lee, W. Leung, J. Ahn, T. Lee, I. S. Park, K. Constant, and K.-M. Ho, Appl. Phys. Lett. **90**, 151101 (2007).
[20]W. Y. Leung, H. Kang, K. Constant, D. Cann, C. H. Kim, R. Biswas, M. M. Sigalas, and K. M. Ho, J. Appl. Phys. **93**, 5866 (2003).
[21]J.-H. Lee, C.-H. Kim, K.-M. Ho, and K. Constant, Adv. Mater. (Weinheim, Ger.) **17**, 2481 (2005).
[22]J.-H. Lee, C.-H. Kim, Y.-S. Kim, K.-M. Ho, K. Constant, W. Leung, and C.-H. Oh, Appl. Phys. Lett. **86**, 204101 (2005).
[23]F. García-Santamaría, E. C. Nelson, and P. V. Braun, Phys. Rev. B **76**, 075132 (2007).
[24]J. B. Pendry, J. Mod. Opt. **41**, 209 (1994).
[25]Z.-Y. Li, Phys. Rev. E **67**, 046607 (2003).
[26]T. Posch, F. Kerschbaum, D. Fabian, H. Mutschke, J. Dorschner, A. Tamanai, and T. Henning, Astrophys. J. Suppl. Ser. **149**, 437 (2003).