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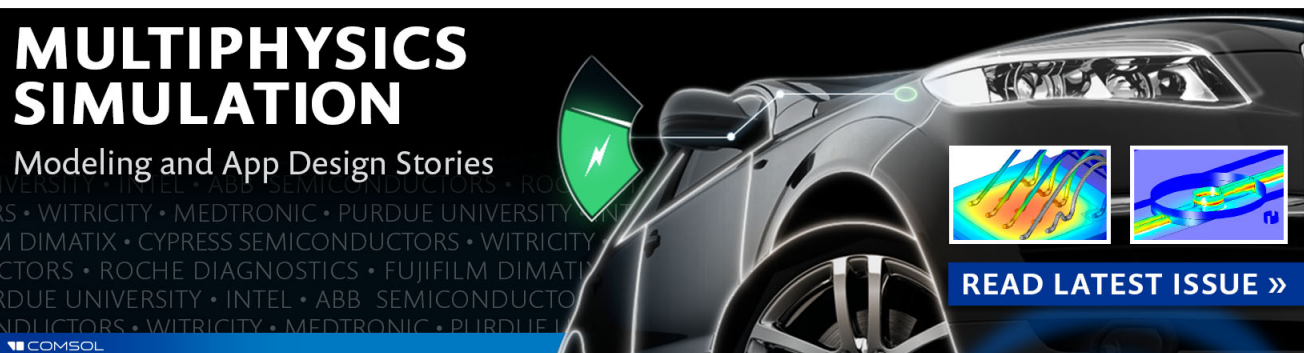Electrotunable in-plane one-dimensional photonic structure based on silicon and liquid crystal
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Layer-by-layer photonic crystal fabricated by low-temperature atomic layer deposition

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Layer-by-layer three-dimensional photonic crystals are fabricated by low-temperature atomic layer deposition of titanium dioxide on a polymer template created by soft lithography. With a highly conformal layer of titanium dioxide, a significantly enhanced photonic band gap effect appears at 3.1 μm in transmittance and reflectance. From optical investigations of systematically shifted structures, the robust nature of the photonic band gap with respect to structural fluctuations is confirmed experimentally. With angle-resolved Fourier-transform spectroscopy, the authors also demonstrate that the fabricated photonic crystal can be a diffraction-free device as the photonic band gap exists over the diffracting regime. © *2007 American Institute of Physics*.
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Electromagnetic wave dispersion of a bulk material can be engineered to have extraordinary properties, such as a full photonic band gap (PBG) in which the propagation of light in all directions is prohibited, provided the bulk material is fabricated into an appropriate periodic structure.[1–3] Also, this periodic structure, called photonic crystal (PhC), can extend the functionalities of photonic or optoelectronic devices through modified photon-matter interactions. However, the modified behaviors are generally observed when the periodicity of the structure is comparable to or smaller than the wavelength of light. As a result, the fabrication of the PhCs for optical applications is, in general, a difficult and demanding task. Among the various PhC structures, the inverse opal structure is most widely studied because its template can be synthesized by the self-assembly of silica or polymer microspheres without multistage, time-consuming procedures.[4,5] A number of techniques, for instance, ceramic slurry infiltration, electrodeposition, and chemical vapor deposition, have been introduced to convert the original opal template to its inverse structures for better optical performance and functionality.[6] Recently atomic layer deposition (ALD) has been used to infiltrate the synthetic opal templates with zinc sulfide,[7] zinc oxide,[8] titanium dioxide (TiO_2),[9] tungsten nitride,[10] and tantalum nitride[11] because the conformal and uniform deposition of various materials is possible with remarkable precision in the thickness of the deposited layer. Theoretically, the full PBG of the inverse opal structures exists only at high frequency bands even for a sufficiently

high refractive index contrast.[12,13] Moreover, the full PBG of the inverse opal structures is destroyed by a structural fluctuation of less than 2% of the lattice constant,[14] which is practically inevitable in fabrication. In contrast, the layer-by-layer structure,[15] often called a woodpile structure, can open the full PBG over the lowest band and is very robust against structural irregularity.[16,17] The advantages of layer-by-layer geometry make the woodpile structure amenable to fabrication by many different techniques, such as semiconductor processing,[18] wafer bonding,[19] microassembly,[20] and direct laser writing.[21]
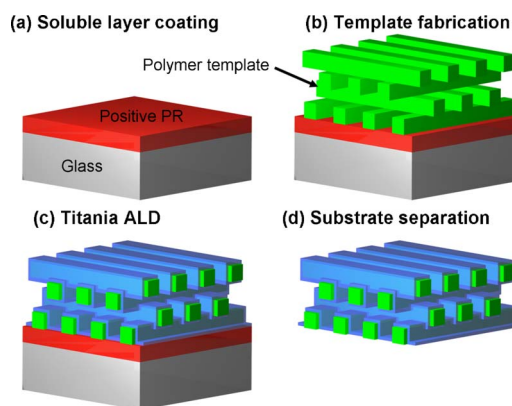

FIG. 1. (Color online) Schematic illustration of the fabrication principle of a TiO_2-coated freestanding photonic crystals by atomic layer deposition. A polymer template is created by soft lithography on a photoresist-coated glass plate and separated from the plate after TiO_2 deposition by atomic layer deposition.
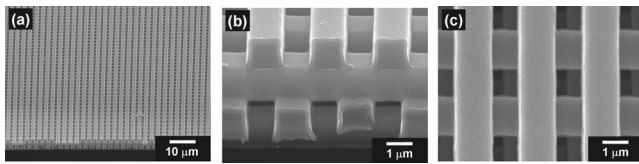
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FIG. 2. Scanning electron microscopy images of a 4×4 mm^2 TiO$_2$-coated freestanding photonic crystal. Side view at (a) lower and (b) higher magnifications and (c) top view. The periodicity (the distance between rods in each layer) is 2.5 μm, and the deposition thickness of TiO$_2$ is 150 nm.
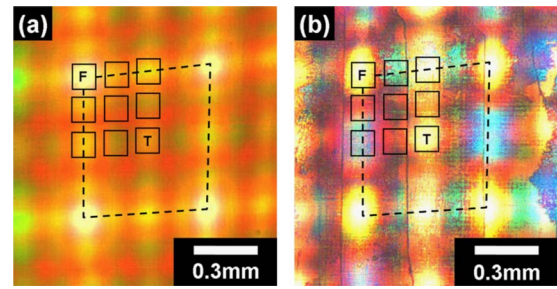

FIG. 3. (Color online) Optical transmission micrographs of moiré fringes of a polymer template (a) before and (b) after TiO$_2$ deposition. The dashed line shows a unit cell of moire fringes and the solid boxes represent the measured areas. Face-centered-tetragonal and tetragonal structures are marked "F" and "T," respectively.

Recently we demonstrated a nonoptical fabrication method of layer-by-layer polymer templates by a soft-lithographic technique[22] and presented theoretical calculations for conformally coated structures with preliminary experimental results.[23] In this letter, we report freestanding woodpile PhCs fabricated by the conformal deposition of amorphous TiO$_2$ on the polymer templates using the ALD technique. Figure 1 schematically illustrates the fabrication method. First, a positive photoresist (AZ®6612, Clariant) is spun on a glass substrate as a sacrificial layer enabling later detachment of the crystal. A polyurethane layer-by-layer template is fabricated on the substrate by a two-polymer microtransfer molding technique,[22] in which a series of layers of ultraviolet (UV)-cured polymer (J91, Summers Optical) rods in an elastomeric mold is transferred and permanently fixed to the desired place by the other UV-curable prepolymer (SK9, Summers Optical) to yield a three-dimensional structure. In our experiment, the polymer template consists of four layers of equally spaced polymer rods, 1.2 μm wide and 1.1 μm high, with a periodicity of 2.5 μm. The orientation of each layer is perpendicular to the layer below. A diffracted moiré fringe-based alignment technique, in which the fringes are monitored at the angle of the first-order diffraction corresponding to the periodicity of the polymer rod,[24] is used. Conformal deposition of TiO$_2$ is performed on the template by ALD at 100 °C with TiCl$_4$ and H$_2$O as precursor and oxidant, respectively. A 150 nm thick TiO$_2$ layer is deposited in 2000 cycles of deposition, where each cycle consists of TiCl$_4$ injection for 0.5 s, N$_2$ purge for 10 s, H$_2$O injection for 10 s, and N$_2$ purge for 30 s. The deposition thickness is optimized for the template to have large PBG in the [001] stacking direction[23] for the dimensions of the polymer template. Since the template fabrication step involves multiple exposures of high-intensity UV light ($\lambda = 366$ nm), the positive photoresist layer is completely dissolvable by a developer. By dipping the coated template in the developer

(AZ®726MIF, Clariant) for 10 min, the coated structure is separated from the substrate. The cross section of the fabricated structure is shown in the scanning electron microscopy (SEM) images in Figs. 2(a) and 2(b) with different magnifications. Fig. 2(b) shows conformally coated TiO$_2$ layer through all layers with a uniform 150 nm thickness around the polymer rods. Moreover, the smooth surface helps reduce undesirable random scattering of light. The SEM image of a misaligned area of the PhC structure in Fig. 2(c) shows all four layers of the PhC, with a gap length between bars reduced from 1.3 to 1.0 μm.

Figure 3 shows the moiré pattern of the same area before and after the TiO$_2$ deposition. To study the tolerance of the band gap to misalignment, test structures were fabricated. We intentionally aligned each layer of the polymer template to have a small domain size as shown in Fig. 3(a) for studying the optical effects from the misalignment. Single domain sizes on the order of mm^2 are usually possible.[25] A single unit cell of the moiré fringes in Fig. 3 is highlighted by dashed lines. The small square boxes depict the areas in which all structures have different alignments with the combinations of 1/4 and 1/2 shift of the periodicity. Note that the structures in the upper left area and the lower right area have face-centered-tetragonal (FCT) (marked as letter "F") and tetragonal (marked as letter "T") structures, respectively. The reflection and transmission spectra have been taken from the nine areas in the boxes in Fig. 3 by a Fourier-transform infrared (FTIR) spectrometer, equipped with a microscope (Hyperion 1000, Bruker). Since the structural variation is less than 8% of the periodicity in a single sampling area,
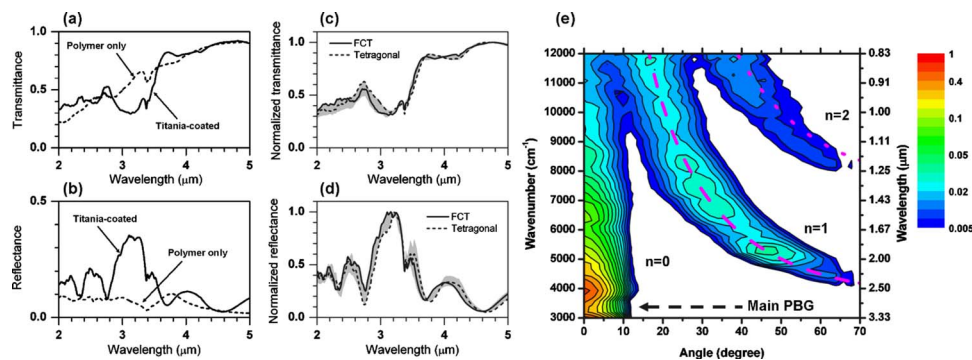
FIG. 4. (Color online) Optical characterization of a four-layer freestanding structure. Changes in (a) transmittance and (b) reflectance of a TiO$_2$-coated FCT structure; variation in (c) normalized transmittance and (d) reflectance spectra by the structural fluctuation; and (e) angle-dependent transmission spectra for a normal incident beam. The dashed and dotted lines in the figure represent first- and second-order diffraction relations.

$100 \times 100 \ \mu\text{m}^2$, we neglected the variation in a single sampling area.

Figures 4(a) and 4(b) show the reflectance and transmittance of a FCT structure before and after the deposition of TiO_2, respectively. The TiO_2-coated structure shows a clear dip in transmission and its corresponding peak in reflection at a region from 2.8 to 3.6 μm, representing a PBG, while the uncoated polymer structure does not, although amorphous TiO_2 has low refractive index close to that of anatase TiO_2 at that optical range.[26,27] The sharp dip at 3.4 μm in transmittance and reflectance originates from an intrinsic absorption band of the polymer, J-91. The changes in transmittance and reflectance due to the misalignment from the FCT structure is shown in Figs. 4(c) and 4(d), based on the measurements of the nine areas in Fig. 3. The gray region shows the difference between maximum and minimum values of reflectance and transmittance taken from all the areas. The spectra of other structures, except FCT and tetragonal structures, are not individually displayed for simplicity. The results confirm the insensitivity to structural fluctuations of the PBG for the woodpile structure[16] although the width of PBG is reduced as much as 15%. We also attempted angle-resolved spectroscopy using a FTIR spectrometer (Magna 760, Nicolet) with a goniometer to measure the degree of scattering at a high frequency region. In the measurement, a sample is mounted on an xy plane with the rods in the structure either parallel or perpendicular to x or y axis while incident angle is fixed on the z axis. The acceptance angle at a certain scanning angle is approximately 10°. The angle-dependent transmission map of the four-layer TiO_2-coated sample is shown in Fig. 4(e), on a logarithmic scale. The transmitted signals are taken every 2° from 0° to 70° to the z axis on the xz plane and normalized to the signal at 0° without the sample. Since the sampling area in the angle-resolved measurements is $1 \times 1 \ \text{mm}^2$, significantly larger than the domain size of the sample, the result reflects the overall scattering characteristics for all different alignments. The result obviously shows significantly scattered light, which follows the diffraction relation $n\lambda = a \sin \theta$. Here n is the diffraction order and a is the distance between adjacent rods, 2.5 μm. The first- and second-order curves are plotted on the color map and the curves are well matched with the angle-dependent transmittance. We experimentally confirm that the main PBG exists out of the diffraction region, and this makes the fabricated structure more useful in practical applications by minimizing stray light. We note that the sum of measured reflection and transmission spectra could be noticeably below unity even for nonabsorbing materials if wavelengths are in the diffraction region, because a diffracted signal is hard to collect by a fixed detector having a finite acceptance angle.

In summary, the fabrication of a layer-by-layer freestanding photonic crystal is demonstrated by atomic layer deposition of TiO_2 on a soft-lithographically fabricated polymer template. Significant enhancement in the PBG effect is observed and is shown to be robust against structural fluctuation as confirmed through a series of measurements of systematically shifted structures. By angle-resolved FTIR spectroscopy, we showed that significant scattering by diffraction exists for wavelengths shorter than the main PBG. Because of the relatively low refractive index and higher extinction coefficient of TiO_2 than other IR materials such as silicon or germanium, it is difficult to open a full PBG in the mid-IR regime. However, the technique presented is still valuable as it is scalable for smaller scale, where TiO_2 is more effective, and various other materials for ALD are available to create advanced functionalities. Moreover, the excellent conformality of the deposited layer can enable further applications, such as optofluidic devices with active materials by removing the polymer template to make a hollow structure.

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