Fabrication of photonic crystals by deep x-ray lithography

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We have developed a new microfabrication technique for the construction of three-dimensional photonic crystals. In particular, we used multiple tilted x-ray lithography exposures in order to construct structures with photonic band gaps in the infrared region. First polymethylmethacrylate (PMMA) resist layers with a thickness of 500 μm were irradiated, then the holes in the resist structure were filled with preceramic polymer and subsequent pyrolysis converts the preceramic polymer into a SiCN ceramic. Theoretical results with fitted values of the dielectric constant are in good agreement with the transmission measurements. © *1997 American Institute of Physics.* [S0003-6951(97)01337-5]

It is now well known that the propagation of electromagnetic (EM) waves in periodic dielectric arrays can be completely forbidden for a certain range of frequencies, the so called photonic band gap (PBG).[1,2] These two-dimensional (2D) or three-dimensional (3D) photonic crystals offer the potential to engineer the properties of the EM waves in these structures.[1,2] The initial interest in this subject came from the proposal to use PBG crystals to inhibit spontaneous emission in photonic devices, leading to more efficient light emitters like thresholdless semiconductor lasers and single mode light emitting diodes.[3–5] However, the difficulties of fabricating smaller scale structures restricted the experimental demonstration of the photonic crystals only to the microwave and the millimeter wave frequency regions.[6–10] There are several applications of the photonic crystals in those frequency regions such as efficient antennas, filters, sources, and waveguides.[1,2,11] There are also several works on the fabrication of 2D photonic crystals in the infrared and visible regions.[12–14]

In this letter, we report the fabrication of 3D photonic crystals with the x-ray lithography technique with a lattice constant of 85 μm and rods diameter of 22 μm. The transmission spectra show a 3D photonic band gap centered at 125 μm (2.4 THz) and are in good agreement with theoretical calculations.

First the process of deep x-ray lithography and the following steps will be briefly explained. Deep x-ray lithography with synchrotron radiation (DXRL) is the first step of the LIGA process.[15] The major steps of the LIGA process are published in details elsewhere.[15,16] X-ray lithography is used in a simple shadow printing process, transferring an absorber pattern into a thick x-ray sensitive polymer (resist). In the subsequent development process, the exposed or unexposed polymer regions are removed, depending on the type of the resist used. Due to the extremely high depth of focus the lateral deviations of the resist walls are as small as 0.05 μm per 100 μm resist thickness. After the development, the gaps of the resist relief are filled with metal via electroplating. The extremely accurate metal form can be used, e.g., for plastic moulding, offering inexpensive microstructure replication. For the fabrication of three-dimensional (3D) microstructures, we modified the first step of the standard LIGA process.[16] Instead of one exposure in the direction perpendicular to the substrate, the resist is exposed several times with different directions of the radiation relative to the mask-resist-assembly. Due to the high depth of focus of DXRL complex microstructures can be fabricated.

The so-called ''three cylinder'' structure[6,17] is well suited for fabrication using the DXRL process. It can be fabricated[18] by three tilted irradiations using a mask with a triangular array of holes in an absorber. Mask and resist must be tilted by 35° with respect to the synchrotron radiation beam. Between the irradiations, the tilted arrangement of mask and resist must be rotated each time by 120°. In Fig. 1

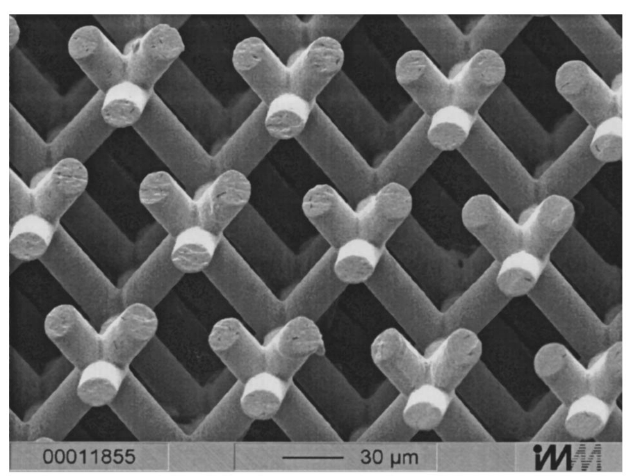

FIG. 1. Photonic crystal made from negative tone resist.

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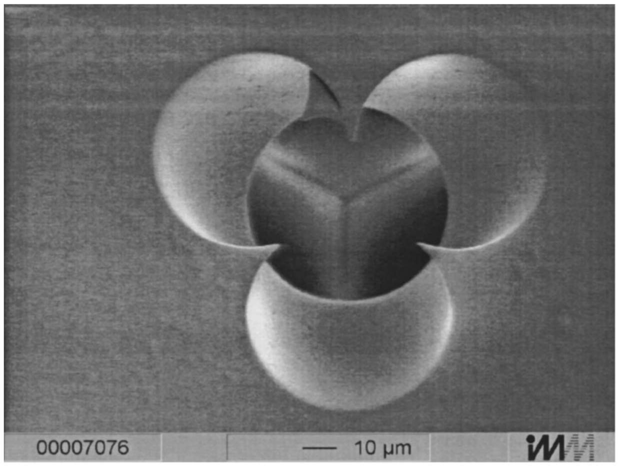

FIG. 2. Intersection of three holes in a photonic crystal made from positive tone resist.

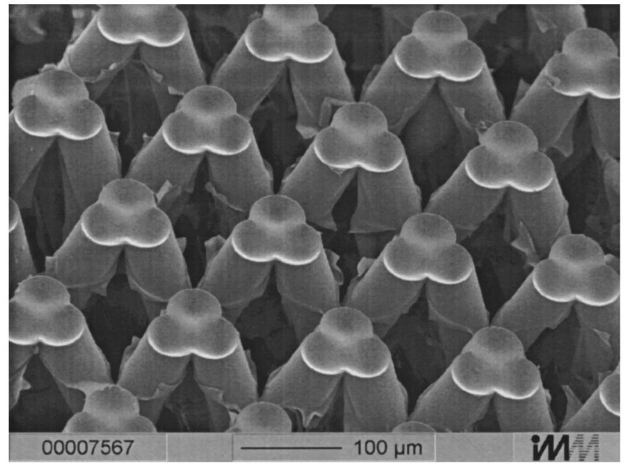

FIG. 3. Photonic crystal made of siliconcarbonitride ceramic.

a photonic crystal with a lattice constant of 114 μm made from negative tone resist is shown. Figure 2 shows the intersection of three holes in a photonic crystal when positive resist is used.

For the three cylinder structure, a complete band gap appears if the refractive index of the cylinders is larger than 2.1.[17] For frequencies within the region of a complete band gap, the propagation of electromagnetic waves is suppressed for all directions in space and all polarizations. Resist materials having a large enough refractive index in the 10 to 200 μm wavelength range are not available yet. Instead, we considered adding a high refractive index ceramic powder in a resist material. Unfortunately, most ceramics have high x-ray absorption coefficients making the pattern transfer in a thick layer difficult.

As a consequence, we have chosen a fabrication process which comprises two main steps. Deep x-ray lithography is used to make mould like the one shown in Fig. 2. This mould is then filled with a ceramic material or a preceramic material.

We first tried to fill the holes with a ceramic slurry but the resist mould could not be filled completely with the ceramic material. We decided to use a preceramic polymer (polyvinylsilazane) which can be transformed into a siliconcarbonitride ceramic by a pyrolysis process.

Since the solution of polyvinylsilazane in tetrahydrofurane (THF) wets the surface of polymethylmethacrylate (PMMA) a complete filling of the microchannels can be achieved by simply putting a drop of solution onto the PMMA structures. After the evaporation of the THF, a solid polymer remains. All process steps must be carried out in an inert atmosphere because the preceramic polymer is sensitive to air and humidity. Prior to the pyrolysis, the polyvinylsilazane must be crosslinked so that it becomes unmeltable. This is simply done by exposure to air. The complicated geometric structure of the fcc crystal precludes the separation of the PMMA from the preceramic polymer. Therefore the PMMA must be removed during the firing as a lost mould. The pyrolysis must be carried out very carefully to minimize crack formation in the ceramic. The delicacy of this process can be understood if one realizes that the transformation of polyvinylsilazane into siliconcarbonitride ceramic is accompanied by a volume shrinkage of about 50%. The samples were pyrolysed at $T = 1100\,°\mathrm{C}$ under nitrogen atmosphere. At least partially crack free ceramics can be obtained if the heating rate does not exceed 5 K/h. A detailed description of the pyrolysis process is given elsewhere.[19] A scanning electron microscope picture of a ceramic photonic crystal is shown in Fig. 3.

We measured the transmission (solid line in Fig. 4) of a structure with lattice constant 85 μm and rods diameter 22 μm. The filling ratio of the ceramic rods in this structure is 35% and the total thickness of the structure is 450 ± 50 μm. There is a constant drop of the transmission which is attributed to the absorption of the ceramic. There is also a well defined drop of the transmission at around 80 cm^{-1} which is related with the first band gap created due to the periodicity of the structure. The gap over the midgap ratio for this stop band is $\Delta\omega/\omega_g = 0.35$.

Theoretical calculations help us to better understand these features. We use the transfer matrix method (TMM), introduced by Pendry and MacKinnon,[20] to calculate the EM transmission through a photonic crystal.[21,22]

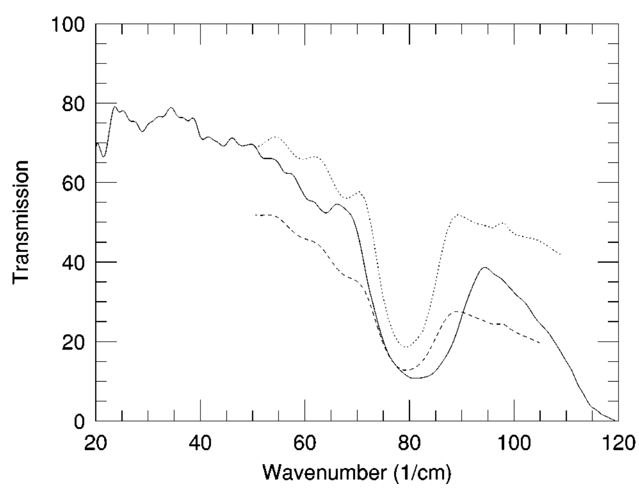

FIG. 4. Measured (solid line) and calculated results for a photonic crystal with 85 μm lattice constant and 22 μm rods diameter. In the calculations, we used a dielectric constant of the rods with real part equal to 3 and imaginary part 0.1 and 0.2 (dotted and dashed lines, respectively).

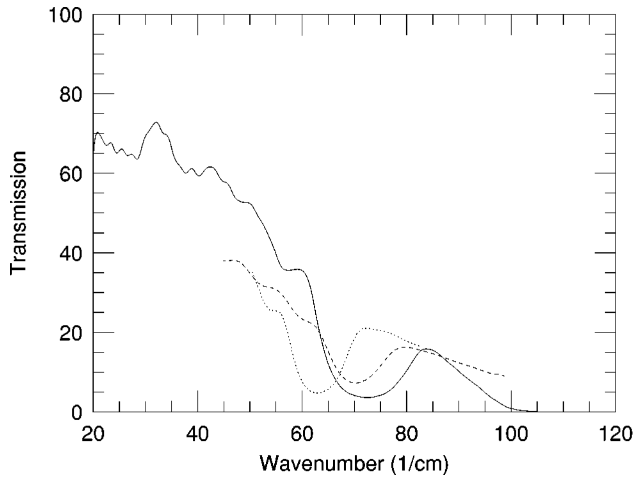

FIG. 5. Measured (solid line) and calculated results for a photonic crystal with 85 μm lattice constant and 31 μm rods diameter. In the calculations, we used a dielectric constant of the rods with imaginary part equal to 0.2 and real part 4 and 3 (dotted and dashed lines, respectively).

The dielectric constant of the SiCN ceramic is not exactly known and as mentioned earlier there are cracks inside the ceramic due to the pyrolysis process. For these reasons, we found an optimum dielectric constant of the ceramic by fitting the calculated values to the measurements. The best fitting was achieved with real part of dielectric constant equal to 3. Using this value, we compare theoretical results for two different values (0.1 and 0.2) of imaginary part of the dielectric constant (dotted and dashed lines in Fig. 4) with the measurements. In the calculations the total thickness of the system is 433 μm. It seems that the measurements can be fitted better with an imaginary part somewhere between 0.1 and 0.2. There are two minor differences between theory and experiment. The first is the measured upper edge of the gap appears at 94 cm^{-1} while the theoretical is at 90 cm^{-1}. The second difference is the much sharper drop of the transmission at higher frequencies in the experimental results than in the calculations. We believe that both difference can be corrected by using a frequency dependent dielectric constant in which both the real and imaginary part increase as the wavenumber increases.

Figure 5 shows transmission measurements (solid line) for a similar photonic crystal with rods diameter 31 μm which corresponds to a filling ratio of 57%. The gap appears at around 70 cm^{-1} with $\Delta\omega/\omega_g = 0.32$. The measurements are compared with two theoretical calculations. In both calculations, the imaginary part of the dielectric constant is 0.2. The real part is 3 and 4 (dashed and dotted lines in Fig. 5). It is clear that the results with real part 3 are in better agreement with the measurements.

In conclusion, it has been demonstrated that x-ray lithography is suitable for the construction of photonic crystals with small lattice constants. The moulding steps required to transform resist crystals into ceramic photonic crystals has also been shown. Theoretical calculations with fitted dielectric constants are in good agreement with measurements. The present microfabrication method is promising for the construction of photonic crystals with band gaps in the optical region.

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[1] See the special issue of the J. Opt. Am. B **10**, 208 (1993) on *Development and Applications of Materials Exhibiting Photonic Band Gaps*.

[2] See the proceedings of the NATO ARW, *Photonic Band Gaps and Localization*, edited by C. M. Soukoulis (Plenum, New York, 1993). For a more recent review, see the articles in *Photonic Band Gap Materials*, edited by C. M. Soukoulis (Kluwer, Dordrecht, 1996).

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