Sol−Gel Organic−Inorganic Composites for 3-D Holographic Lithography of Photonic Crystals with Submicron Periodicity

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In the decade following the development of the theory of photonic band gaps,[1,2] particular attention has been devoted to the fabrication of periodic structures with gaps at visible and near-infrared energies. Because of their ability to efficiently trap,[3] reflect,[4] and guide[5] light in three dimensions around sharp angles, photonic crystals designed for optical wavelengths are expected to replace low-curvature passive waveguides and to greatly increase the component density of integrated optical circuits. Structures with micron and submicron periodicities have been successfully constructed through lithographic (X-ray,[6] electron,[7] laser vapor deposition,[8] and two-photon[9]) methods. In these techniques, the lithographic beam sequentially inscribes each element or “point” of the lattice. Progress has also been made with spontaneous self-organization routes to inverse opal structures, which are cast from colloidal-sphere templates;[10a−c] recent advances in this field[11a,b] have significantly decreased the densities of growth defects in these replicas, which generally exhibit fcc symmetry and submicron periodicity.

Our group has recently demonstrated that ordered structures with the submicron lattice constants required for band gaps at visible wavelengths can be defined in a single, rapid (6-ns) step through three-dimensional holographic lithography (3-D HL).[12,13] This method avoids the fractures and stacking faults that are frequently found in structures obtained by self-assembly and, in principle, allows for the fabrication of defect-free photonic crystals. In 3-D HL, a photosensitive film is patterned, within the duration of a single optical pulse, by the intensity modulations that arise from the interference of four noncoplanar UV laser beams. The translational symmetry of this pattern is determined by the differences between the four laser wavevectors, and its primitive basis (i.e., the unit repeated at each lattice point) can be controlled through the intensity and polarization parameters. Both face- and body-centered cubic structures have been created by this technique from SU-8, a commercially available epoxy photoresist.[12]

In addition to 3-D connectivity and submicron periodicity, a refractive index greater than 2 is necessary to open omnidirectional band gaps in photonic crystals. Because of the relatively small refractive index of the organic SU-8 polymer ($n = 1.6$), structures formed in this material do not exhibit complete band gaps. Instead, they have been used as templates for inorganic structures with larger index contrast.[12] However, the templating process can lead to shrinkage-induced fractures that disrupt long-range order. In principle, this drawback can be avoided by directly patterning inorganic substrates. Indeed, the formation of holographic gratings has been demonstrated in germanosilicate[14] and chalcogenide (AsSeTe)[15] films. However, these materials are unsuitable for 3-D holographic lithography because they absorb strongly at the lithographic wavelength;[14,15] the consequent attenuation of the optical interference pattern would disrupt the lattice symmetry or even prevent pattern formation through the depth of the film.

Here, we show that the attractive properties of organic photoresists (efficient photoresponse, transparency, and ease of processing into thin films) and inorganic materials (mechanical and thermal stability, high refractive index) can be combined in organic−inorganic composites, which belong to the class of organically modified silica (ORMOSIL) materials pioneered by the research group of H. Schmidt.[16] The silica−acrylate composites (SACs) that we use are derived from the sol−gel processing of methacrylate-substituted silicon and transition metal (Zr, Ti) alkoxide precursors. Macroscopic separation between the organic and inorganic phases is prevented in the SAC system

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(1) Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059.

(2) John, S. *Phys. Rev. Lett.* **1987**, *58*, 2486.

(3) Foresi, J. S.; Villeneuve, P. R.; Ferrera, J.; Thoen, E. R.; Steinmeyer, G.; Fan, S.; Joannopoulos, J. D.; Kimerling, L. C.; Smith, H. I.; Ippen, E. P. *Nature* **1997**, *390*, 143.

(4) Joannopoulos, J. D.; Villeneuve P. R.; Fan S. *Nature* **1997**, *386*, 143.

(5) Lin, S.-Y.; Chow, E.; Hietala, V.; Villeneuve P. R.; Joannopoulos, J. D. *Science* **1998**, *282*, 274.

(6) Lin, S.-Y.; Fleming, J. G.; Hetherington, D. L.; Smith, B. K.; Biswas, R.; Ho, K. M.; Sigalas, M. M.; Zubrzycki, W.; Kurtz S. R.; Bur J. *Nature* **1998**, *394*, 251.

(7) Krauss, T. F.; De La Rue R. M.; Brand, S. *Nature* **1996**, *383*, 699.

(8) Wanke, M. C.; Lehmann, O.; Müller, K.; Wen Q.; Stuke, M. *Science* **1997**, *275*, 1284.

(9) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I.-Y. S.; McCord-Maughon, D.; Qin, J.; Rockel, H.; Rumi, M.; Wu, X.-L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51.

(10) (a) Zakhidov, A. A.; Baughman, R. H.; Iqbal, Z.; Cui, C.; Khayrullin, I.; Dantas, S. O.; Marti, J.; Ralchenko, V. C. *Science* **1998**, *282*, 897. (b) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802. (c) Johnson, S. A.; Ollivier, P. J.; Mallouk, T. E. *Science* **1999**, *283*, 963.

(11) (a) Vlasov, Y. A.; Bo, X.-Z.; Sturm, J. C.; Norris, D. J. *Nature* **2001**, *414*, 289. (b) Griesebock, B.; Egen, M.; Zentel, R. *Chem. Mater.* **2002**, *14*, 4023.

(12) Campbell, M.; Sharp, D. N.; Harrison, M. T.; Denning, R. G.; Turberfield, A. J. *Nature* **2000**, *404*, 53.

(13) Turberfield, A. J. *MRS Bull.* **2001**, *26*, 632.

(14) Albert, J.; Malo, B.; Johnson, D. C.; Bilodeau, F.; Hill, K. O.; Brebner, J. L.; Kajrys, G. *Opt. Lett.* **1993**, *18*, 1126.

(15) Meneghini, C.; Villeneuve, A. *J. Opt. Soc. Am. B* **1998**, *15*, 2946.

(16) Krug, H.; Tiefensee, F.; Oliviera, P. W.; Schmidt, H. *Proc. SPIE Int. Opt. Eng.* **1992**, *1758*, 448.

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because the methacrylate moieties remain covalently bound to the Si and transition metal centers of the siloxane and metal oxide networks, respectively. During 3-D HL, photoinitiated free-radical polymerization of olefin substituents causes localized structural densification that renders irradiated areas of the composite insoluble in common organic solvents. Unexposed regions can then be dissolved away to bring into relief periodic structures with high inorganic content. Although a selection of passive, integrated optical elements have been fabricated through phase,[17] photomask,[18−20] contact-printing,[21] and 2-D interference lithography[22] of ORMOSILS, these have generally been planar, 2-D structures with low resolution and aspect ratios and low-contrast refractive-index profiles. We report here that sol−gel-derived silica−methacrylate composites doped with transition metal oxide particles are suitable for the photolithography of complex 3-D structures with submicron periodicities and large inorganic contents suitable for use as photonic crystals at optical frequencies.

SAC colloids were formed by initiating the hydrolysis and condensation reactions of 3-methacryloxypropyltrimethoxysilane with 0.05 M HCl at a [H_2O]/[alkoxide group] ratio $R = 1.5$. For our purposes, it is necessary to form weakly branched, oligomeric siloxanes that mutually interpenetrate without “sticking”[23] during spin-casting to form optical-grade films with negligible Rayleigh scattering. A relatively low R value and acidic reaction conditions were therefore chosen to minimize condensation reactions that lead to highly cross-linked, particulate silica.[24] Condensation reactions are further inhibited by the propyl methacrylate substituent, which decreases the number of reactive alkoxides (from four to three); imposes steric hindrance on the condensation reaction, which is a nucleophilic substitution; and engages in H-bonding with Si−OH groups through its C═O functionality.[27] Collectively, these factors lead to the formation of siloxane oligomers. Solution ^{29}Si NMR spectra of the siloxanes were dominated by T_1 (−52.0 ppm) and T_2 (−58.8 ppm) species, which are characteristic of weakly branched oligomers. The ν_{as}(Si−O−Si) vibrational mode corresponding to the siloxane chains was observed at 1080 cm^{-1} in FT-IR spectra. Electrospray mass spectrometry indicated that the oligomers were predominantly linear with a maximum m/z = 1079.80 ionized with Na^+, which corresponds to siloxanes with five Si centers. The siloxane system was doped with varying amounts (0.1−0.3 molar equiv per silicon atom) of a 1:1 zirconium(IV) *n*-propoxide [or titanium(IV)] isopropoxide/methacrylic acid complex. The transition metal alkoxide complex reacts stoichiometrically with H_2O[25] in the reaction mixture to form 2−4-nm methacrylate-capped zirconia clusters.[26] The transition metal oxide particles were added to increase the refractive index[27] and the flexural strength of the composite. They are also known to improve the cross-linking efficiency of methacrylate-substituted siloxane chains.[25,28] Thermal gravimetric analysis (11−1000 °C at 20 °C min^{-1} under an air flow of 50 mL min^{-1}) showed that a composite, doped with only 0.1 molar equiv per Si of the zirconium(IV) *n*-propoxide/methacrylic acid complex, consisted of 35 wt % inorganic oxide. The sol is transparent at wavelengths between 280 and 800 nm. (The $\pi \rightarrow \pi^*$ excitation of the conjugated ester carbonyl of the methacrylate substituent gives rise to an absorption maximum at 245 nm.[29,30]) The photoinitiator 2,2-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651) was incorporated (at 1 wt %) to sensitize the SAC to 355-nm radiation; this introduced a negligible (3%) absorption loss at this wavelength.

For 3-D HL, 6-μm-thick SAC films were spin-cast as solutions onto glass microscope cover slips ($d = 2.25$ cm). The glass substrate was index-matched with lens oil to a poly(methyl methacrylate) mount to prevent back-reflection before exposure to a single pulse (6 ns, 90 mJ cm^{-2}) of the interference pattern. The optical assembly for 3-D HL has been detailed elsewhere.[12] Briefly, four mutually coherent beams are created by splitting the output of a frequency-tripled Nd:YAG laser. The central beam is normal to the sample interface, while the other three beams are symmetrically positioned azimuthally, making an angle of 38.9° to the normal. The differences between the wavevectors of the central beam ($k_o = 2\pi/d[\bar{3}/2\ \bar{3}/2\ \bar{3}/2]$) and those of its peripheral beams ($k_1 = 2\pi/d[\bar{5}/2\ \bar{1}/2\ \bar{1}/2]$, $k_2 = 2\pi/d[\bar{1}/2\ \bar{5}/2\ \bar{1}/2]$, $k_3 = 2\pi/d[\bar{1}/2\ \bar{1}/2\ \bar{5}/2]$) generate a bcc unit cell in reciprocal space, which in real space translates into a 3-D intensity variation with fcc symmetry and a lattice parameter of 922 nm.

During the exposure, photoinitiator molecules undergo α-cleavage to produce benzoyl free radicals, which initiate polymerization of the methacrylate groups primarily in regions of high intensity. In the FT-IR spectrum of the irradiated film, polymerization is indicated by the decrease in intensity of the ν(C═C) vibrational mode at 1638 cm^{-1}. Films of SAC doped with 0.1 molar equiv per Si of the zirconium(IV) *n*-propoxide/methacrylic acid complex have an index of refraction of 1.512, which increases to 1.527 upon exposure to UV light.[27] Because of this difference in refractive index between polymerized and unpolymerized regions, the exposed area (with a diameter of ∼1 cm) is slightly iridescent. Iridescence is greatly enhanced by immersing the film in 2-propanol to extract unpolymerized material

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(17) Fardad, M. A.; Touam, T.; Meshkinfam, P.; Sara, R.; Du, X. M.; Andrews, M. P.; Najafi, S. I. *Electron. Lett.* **1997**, *33*, 1069.

(18) Li, C.-Y.; Chisham, J.; Andrews, M. P.; Najafi, S. I.; Mackenzie, J. D.; Peyghambarian, N. *Electron. Lett.* **1995**, *31*, 271.

(19) Coudray, P.; Chisham, J.; Andrews, M. P.; Najafi, S. I. *Opt. Eng.* **1997**, *36*, 1234.

(20) Blanc, D.; Pelissier, S.; Saravanamuttu, K.; Najafi, S. I.; Andrews, M. P. *Adv. Mater.* **1999**, *11*, 1508.

(21) Mallouk. A. P.; Rantala, J. T.; Honkanen, S.; Mendes, S. B.; Peyghambarian, N. *Opt. Commun.* **1999**, *162*, 215.

(22) Shishido, A.; Diviliansky, I. B.; Khoo, I. C.; Mayer, T. S.; Nishimura, S.; Egan, G. L.; Mallouk, T. E. *Appl. Phys. Lett.* **2001**, *79*, 3332.

(23) Brinker, C.; Scherer, G. *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academic Press: New York, 1990; Chapter 8.

(24) Brinker, C.; Scherer, G. *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academic Press: New York, 1990; Chapter 2.

(25) Schubert, U.; Völkel, T.; Moszner, N. *Chem Mater.* **2001**, *13*, 3811.

(26) Krug, H.; Tiefensee, F.; Oliviera, P. W.; Schmidt, H. *Proc. SPIE Int. Opt. Eng.* **1992**, *1758*, 448.

(27) Saravanamuttu, K.; Du, X. M.; Najafi, S. I.; Andrews, M. P. *Can. J. Chem.* **1998**, *76*, 1717.

(28) Trimmel, G.; Fratzl, P.; Schubert, U. *Chem. Mater.* **2000**, *12*, 602.

(29) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966; pp 247−268.

(30) Rao, C. N. R. *Ultra-Violet and Visible Spectroscopy, Chemical Applications*, 3rd ed.; Butterworths: London, 1974; pp 42−47.

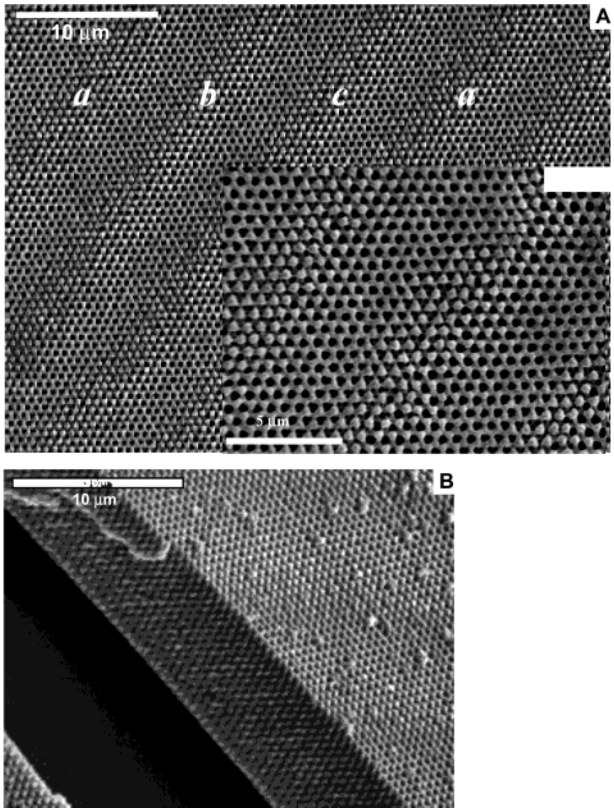

Figure 1. Scanning electron micrographs of (A) the top surface of the patterned SAC film showing the *abca* banding of (111) planes and (B) its (11$\bar{1}$) cleavage plane.

(Figure 1D). The microperiodic structures were characterized through both scanning electron microscopy and laser-scanning confocal microscopy.

Figure 1 contains scanning electron micrographs of the top surface of the patterned film, which closely approximates the (111) plane of the fcc structure. Because the film surface is not exactly coplanar with the (111) plane of the interference pattern, the surface intersects the unit cell of the fcc interference pattern at a position that changes monotonically across the film. The result is a periodic pattern of broad bands on the film surface that correspond to the intersection of the surface with different (111) planes stacked in the characteristic *abca* sequence.

The structural basis (“atom”) that is repeated at each lattice point consists of a roughly ellipsoidal volume of dielectric with its long axis oriented along the [111] direction. The top and base of each basis branches into three “bonds” that link it to its nearest neighbors in the (111) planes above and below it. The light bands in Figure 1A correspond to areas where the film surface has cut through the middle of a layer of atoms. These are flanked by darker bands where the surface has cut through the bonds that link atoms in the adjacent (111) planes. Bonds to the underlying layer are also visible in the gaps between atoms (inset). A scanning electron micrograph of the (11$\bar{1}$) cleavage plane (Figure 1B) shows that 13 (111) planes are linked in this way to form the expected stacking sequence. Moreover, the film appears to be uniformly patterned throughout its 6-μm depth, indicating that the optical interference pattern is not modified by significant attenuation within the thickness of the film. The average “interatomic” distance of 625 nm in the (111) surface of the patterned structure corresponds well to that (652 nm) of the optical interference pattern. The interplanar distance of ~500 nm in the patterned structure is consistent with the expected refraction of the writing beams at the film surface, which stretches the interference pattern along the [111] direction.

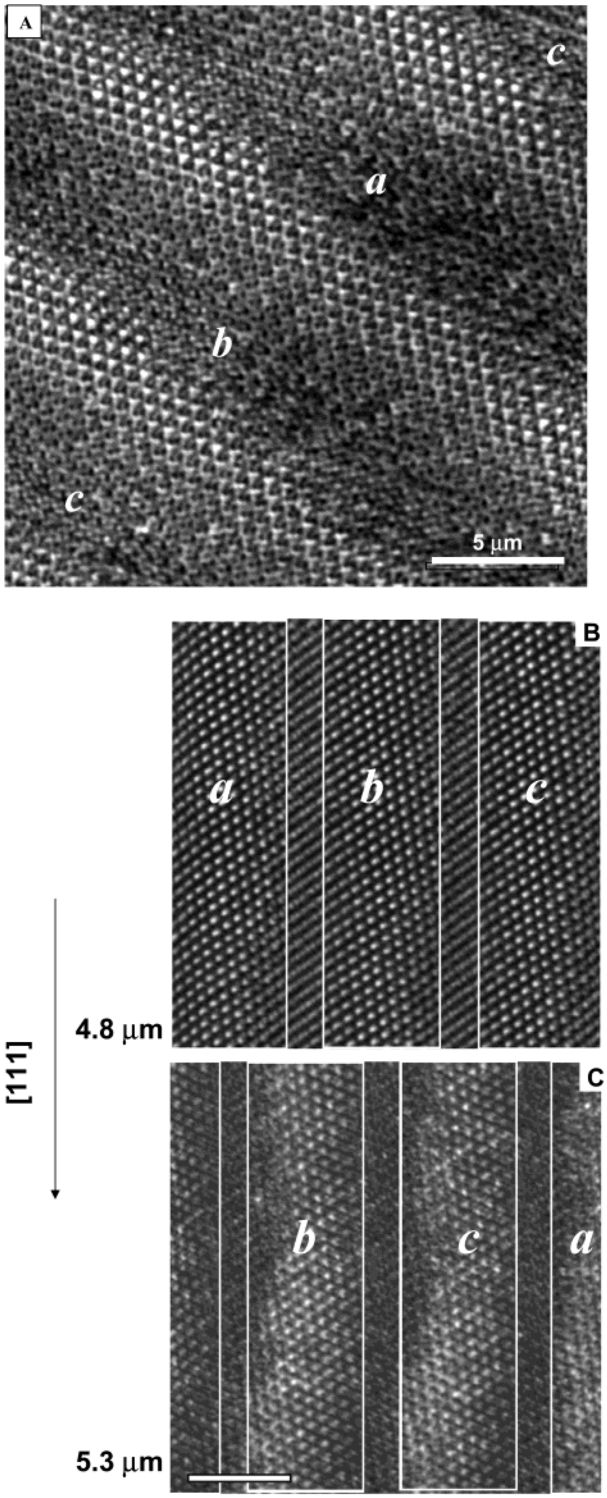

Figure 2. (A) Laser scanning confocal micrograph of the (111) planes at a depth of 1.2 μm from the free surface of the SAC film. (B,C) Confocal micrographs showing the translations ($a \rightarrow b$, $b \rightarrow c$, and $c \rightarrow a$) of the (111) planes at a vertical interval of 500 nm.

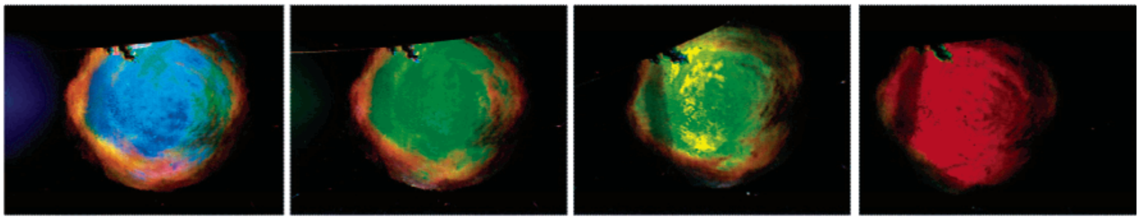

Figure 3. Optical micrographs showing diffraction of a collimated beam of white light, incident at various angles to the patterned region (~0.8 cm^2) of the SAC film.

The scanning electron micrographs in Figure 1 provide topological evidence that the symmetry and submicron periodicity of the optical interference pattern is reproduced at the (111) and (11$\bar{1}$) cleavage plane *surfaces*. We confirmed that this lattice structure is reproduced throughout the entire *volume* of the patterned region by acquiring laser scanning confocal images at different focal planes through the depth of the film. For example, the reflection-mode confocal micrograph in Figure 2A, which was acquired at a depth of 1.2 μm from the free surface of the film, corresponds to a (111) plane of the fcc structure with the expected interatomic spacing of 625 nm. The micrograph also shows the same periodic banding as observed at the surface of the film (Figure 1), which is due to slight misalignment of the focal planes relative to the (111) direction. Here, the lighter bands between the (111) planes of atoms (labeled *cabc*) clearly show the triangular cross sections of the sets of three bonds that project upward from each lattice point to link to neighbors in the plane adjacent to the one that is in focus.

A series of confocal micrographs acquired along the [111] direction from the free surface of the film showed the *abca* packing sequence of the (111) planes. Parts B and C of Figure 2 form part of this series and were acquired at depths of 4.8 and 5.3 μm, respectively, to show the translations ($a \rightarrow b$, $b \rightarrow c$, and $c \rightarrow a$) of the (111) planes that take place at a vertical interval of 500 nm.

The optical micrographs in Figure 3 show diffracted colors of a collimated beam of white light, incident at various angles to the patterned SAC film surface. The color remains uniform across the film, signifying that the structure retains its spatial coherence throughout the ~0.8 cm^2 patterned area and that it is free of macroscopic defects. This contrasts with the characteristic multicolored iridescence caused by macroscopic fractures, stacking faults, and polycrystallinity that is commonly observed in structures obtained by template reactions based on self-assembled spheres.[10a,b] Moreover, the SAC structured films remain attached to their glass substrates, are mechanically robust, and remain stable under ambient conditions for over 9 months.

SAC materials are capable of achieving the high lithographic resolution required to make photonic crystals with submicron unit cells. In the case of the fcc structure, the high resolution is illustrated by the clear definition of the bonds at each lattice point, which are only ~150 nm wide. Lithographic resolution on this scale is not possible with commercially available organic−acrylate monomer-based formulations. When these were exposed to the 3-D holographic pattern, periodic surface relief was observed, together with fracture surfaces that betrayed the presence of periodic strain modulations within the sample, but it proved impossible to remove the less dense material by treatment with solvents.[31] We attribute this loss of feature contrast to inadequate spatial confinement of free-radical propagation in the growing polymer. By contrast, diffusion of free-radical propagators is strongly suppressed in SAC because methacrylate groups are covalently bound to siloxane and zirconia networks, which themselves impose additional steric hindrance on organic chain growth.[27] Because the polymerization is spatially confined and localized in this way, the necessary submicron resolution can be achieved.

In conclusion, we have demonstrated that sol−gel-derived silica−methacrylate composites doped with transition metal oxide clusters are suitable for the *direct* 3-D HL of ordered structures with high inorganic oxide contents (>35 wt %). SAC composites with only 0.1 molar equiv per Si of the zirconium(IV) *n*-propoxide/methacrylic acid precursor have an index of refraction of 1.527. This value is greater than the refractive indices of both commercially available simple acrylate photoresists (~1.48) and pure silica (~1.47). By increasing the amount of transition metal-oxo oligomers, it is possible to increase the refractive index of the composites to values >2,[32] as would be required for photonic crystals that exhibit complete band gaps. Significantly, this approach is template-free and will allow the direct fabrication of 3-D photonic crystals where the refractive index can be controlled through the careful variation of the inorganic component of sol−gel-derived photosensitive composites.

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[31] Campbell, M.; Sharp, D. N.; Harrison, M. T.; Denning, R. G.; Turberfield, A. J. Oxford University, Clarendon Laboratory. Unpublished results, 1998.

[32] Mennig, M.; Oliveira, P. W.; Schmidt, H. *Thin Solid Films* **1999**, *351*, 99.