High filling fraction gallium phosphide inverse opals by atomic layer deposition

E. Graugnard,[a] V. Chawla, D. Lorang, and C. J. Summers[b]
School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

(Received 21 June 2006; accepted 25 September 2006; published online 20 November 2006)

High filling fraction gallium phosphide (GaP) inverse opals were fabricated by atomic layer deposition within the void spaces of silica colloidal crystal templates. Depositions were performed from 400 to 500 °C using trimethylgallium and tris(dimethylamino)phosphine precursors. The resulting films were characterized by optical reflectance, which indicated infiltration as high as 100% of the conformal film growth maximum, corresponding to a volume filling fraction of 0.224. X-ray diffraction measurements confirmed the crystallinity of the film. These results indicate the fabrication of three-dimensional photonic crystals using a III-V optoelectronic material with sufficient dielectric contrast to form a full photonic band gap in the visible. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2387874]

Photonic band gap devices offer tremendous potential for controlling the emission rates and propagation of light by creating microcavity and waveguide structures with extremely high Q factors and low loss.[1] For three-dimensional (3D) photonic crystal structures with a sufficiently high dielectric contrast and appropriate crystal symmetry, an omnidirectional or full photonic band gap (FPBG) will exist within the crystal, which forbids the propagation of light within a certain range of frequencies.[2,3] In order to form a full photonic band gap in opal-based photonic crystals, the face-centered-cubic lattice must be inverted and possess a refractive index contrast greater than 2.8 for full infiltration (26% of volume) and 3.3 for complete conformal infiltration (22.4% of volume).[4,5] To achieve these requirements, infiltration techniques have been developed for depositing high refractive index material within the pores of an opal template which is subsequently removed to create an inverted lattice of air spheres in a high index backbone. Inverse opals with full gaps in the infrared have been fabricated using Si, Ge, GaAs, and InP,[6–11] while other materials, including SnS_2, Sb_2S_3, GaP, and Ta_3N_5,[12–15] have been investigated because they offer the potential to form FPBGs in the visible.

Inverse opals fabricated from III-V materials are technologically important due to the possibility of manipulating their intrinsic optoelectronic properties, while also utilizing those properties to create active photonic devices. However, for GaP, which has both high index and transparency in the visible spectral region, only low filling fractions or anomalous behavior of the infiltrated material have been reported.[14,16] In the first study reported by Romanev *et al.* using a cyclic chemical vapor deposition method with long (several hours) precursor hold times,[16] the GaP filling fraction was only ~3%, insufficient to form an inverse lattice.[17] Using a similar cyclic chemical vapor deposition technique, Palacios-Lidón *et al.* obtained higher filling fractions, but the infiltrated GaP exhibited anomalous optical behavior resulting from a topology of spherical GaP grains within the opal void spaces, deviating from surface limited growth.[14] Although the resulting inverse lattice deviated from a typical inverse opal, certain structural parameters for the spherical GaP topology were predicted to result in a FPBG.

In this letter, we report the fabrication of high filling fraction GaP inverse shell opals by atomic layer deposition (ALD) and show the potential of GaP as a high index, transparent material for photonic crystals. In previous work, ALD of thin dielectric films has proven to be a powerful tool for fabricating single and multicomponent inverse opals due to its high precision and surface limited conformal growth characteristics.[15,18–21] Using ALD, GaP filling fractions as high as 100% of the conformal film growth maximum were achieved, and the inverse lattices were consistent with surface limited film growth. The optical properties were in excellent agreement with photonic band calculations, indicating that the formation of a full 3D photonic band gap should be possible.

Opal films were formed on silicon substrates by forced self-assembly of silica spheres within a 10 μm thick confinement cell. The sphere diameters ranged from 297 to 450 nm, resulting in face-centered-cubic films consisting of approximately 40–27 sphere layers, respectively, oriented with the $\langle 111 \rangle$ direction normal to the substrate. The samples were infiltrated with a custom ALD reactor operated in the fill-hold-purge mode to enhance precursor diffusion and efficient precursor usage. In this mode, sequential precursor pulses were delivered to the reaction chamber to a predetermined partial pressure, held for a fixed time, and then purged from the chamber. GaP ALD has been reported previously using metal organic and hydride precursors.[22–26] However, in this study, optimal surface limited growth on SiO_2 opal templates was performed at 450 °C using trimethylgallium (TMGa) and tris(dimethylamino)phosphine (TDMAP), which is a metal organic alternative to PH_3 with a far lower toxicity level.[27] The TMGa pulses were held for 10 s at a partial pressure of 300 mTorr and then purged with 300 SCCM (SCCM denotes cubic centimeter per minute at STP) of nitrogen for 20 s. The TDMAP was held for 10 s at 100 mTorr and then purged for 60 s. A longer purge time for TDMAP was used since its vapor pressure (3.5 Torr at 20 °C) is

[a]Current address: Dept. of Engineering-Physics-Systems, Providence College, Providence, RI 02918–0001.
[b]Electronic mail: chris.summers@mse.gatech.edu

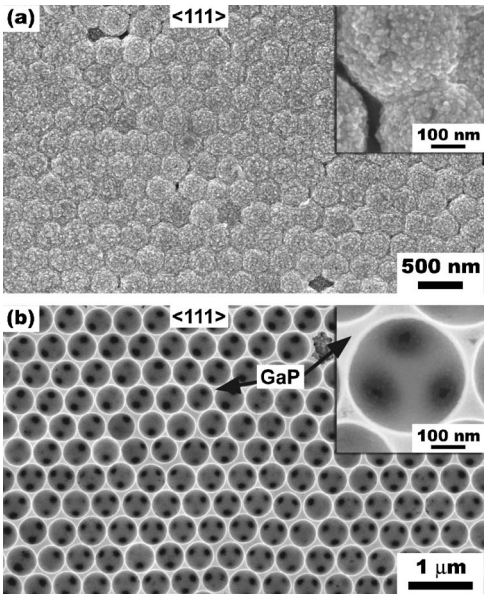

FIG. 1. (a) SEM image of the top surface of a 297 nm GaP infiltrated opal showing conformal, polycrystalline film growth. The inset shows a higher magnification image at a small gap between spheres, selected to reveal the conformal film growth. (b) Cross section through (111) plane of a 450 nm inverse opal. The shell-like structure of the GaP film confirms the conformal nature of the growth mode. The inset shows details of the air cavity structure and the high quality of the conformal GaP backbone for a 350 nm inverse opal.

much lower than TMGa (182 Torr at 20 °C). During the nitrogen purges, the pressure within the reactor was ~1 Torr.

Figure 1(a) shows a scanning electron microscopy (SEM) image of the top surface of a 297 nm GaP infiltrated opal after 100 ALD cycles. The GaP film is polycrystalline with a fine scale (<10 nm) grain structure and is conformal to the spherical surfaces, as can be seen from the growth in the regions of missing spheres. The inset shows a high magnification image at a small gap between neighboring spheres, specifically selected to illustrate the fine conformal grain structure. This film morphology is similar to opals infiltrated with ZnS by ALD at 500 °C, which also grows as a polycrystalline film.[28] The infiltrated opal was ion milled to obtain access to the silica sphere network and was etched three times in 2% HF for 15 min to remove completely the silica spheres, as confirmed when the Bragg peak ceased to shift to a shorter wavelength. Figure 1(b) shows the ion-milled cross section of a 450 nm inverse opal midway through the outermost (111) plane of spheres. The lattice consists of spherical air cavities within a GaP backbone grown with 300 ALD cycles. The conformal nature of the GaP film growth is confirmed by the shell-like structure observed in the image, which leaves small air pockets at the interstitial points between the spheres and is predicted to enhance the photonic properties.[4,5] Nonconformal growth is not surface limited and would have completely filled these void regions, as observed in the metal organic chemical vapor desposition growth reported previously.[14] The dark spots observed within the cavities result from the contact points of the silica spheres and provide the connectivity pathway for the lattice. These connection pores, ~30 nm in diameter, and air pockets at the interstitials are shown in the high magnification inset, which shows the high structural quality of the conformal GaP shell for a 350 nm inverse opal. The backbone

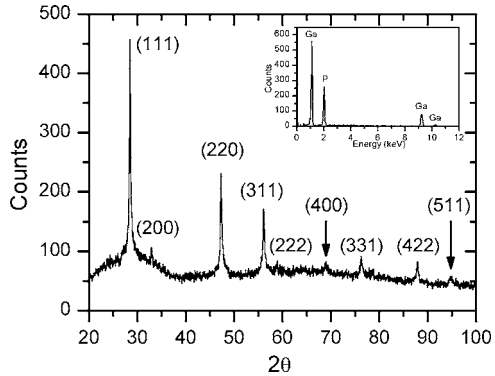

FIG. 2. X-ray diffraction data for a GaP inverse opal. Labeled diffraction peaks agree in both position and intensity with published data, confirming the cubic GaP crystal structure. The inset shows an energy dispersion spectrum for an inverse opal, confirming the presence of only Ga and P within the lattice.

structure exactly conforms to that expected for surface limited template-patterned polycrystalline film growth.

The crystal structure of a GaP film deposited on a fused silica substrate was assessed by x-ray diffraction measurements, and the resulting data are plotted in Fig. 2. The x-ray diffraction data show clear peaks matching the intensity and position of the diffraction pattern reported for bulk GaP, confirming the cubic $F(-4)3m(216)$ phase of the film. The inset of Fig. 2 shows an x-ray energy dispersion spectrum acquired at 20 keV for the 450 nm inverse opal, confirming the presence of only Ga and P in the inverse backbone.

The specular reflectance of the 450 nm GaP inverse opal film, plotted in the right panel of Fig. 3, displayed a Bragg peak at 1.0 eV (1245 nm or a normalized frequency of 0.51) with a peak width (full width at half maximum/E_{Bragg}) of 22%. The spectrum was acquired using a microreflectivity system with a spot diameter of ~100 μm. Reflected light was routed through a vis-IR spectrometer to an InGaAs photodiode detector. The data are compared to a full photonic band calculation, performed using the MIT PHOTONIC BAND package,[29] for a GaP inverse opal having a conformal infiltration of 100% and a refractive index of 3.34 (GaP index at 600 nm).[30] The calculated gap between the second and third

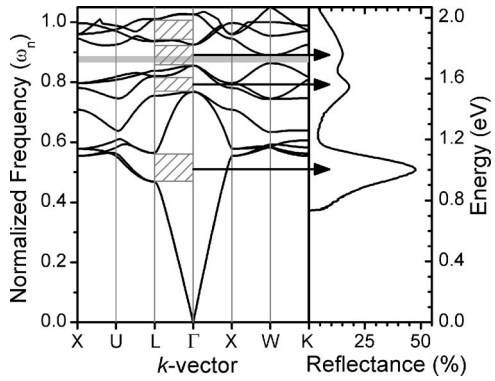

FIG. 3. Photonic band structure calculated for a conformal filling fraction of 0.224 (complete conformal infiltration) compared to the measured reflectance spectrum from a 450 nm GaP inverse opal. As indicated by arrows, the measured spectrum agrees very well with the calculated gap positions and widths, shaded in gray along the Γ-*L* direction. The solid gray bar indicates the ~3% full photonic band gap of the structure. The excellent agreement between the calculated bands and measured reflectance directly confirms the high GaP filling fraction.

bands was centered at a normalized frequency of 0.516 with a gap width of 18.5%. The peak width of the measured spectrum is slightly larger than the calculated width and is typically broadened by disorder within the opal. The reflectance of the Bragg peak in the inverse opal was 48%, which is lower than the initial opal reflectance of 70%. We attribute the low reflectance to scattering from the polycrystalline film and are currently investigating annealing procedures to reduce surface roughness as well as techniques to produce opal templates with a higher initial optical quality. The sharp decrease in spectral intensity below 0.75 eV corresponds to the spectral limit of the detector. However, the measured spectrum agrees very well with the calculated band structure (and the Bragg-Snell equation), confirming the conformal nature of the GaP growth and giving an infiltration of 100% or filling fraction of 0.224. Two higher energy peaks were also observed at 1.55 and 1.76 eV and closely matched high-order gaps in the calculated band structure. The calculation also indicates a FPBG at a normalized frequency of 0.88, as determined by the eighth and ninth bands at the *W* point.[5] The excellent agreement between the measured and calculated band structures implies that a full photonic band gap of ~3% may exist at 726 nm.

In summary, we have reported the fabrication of high filling fraction GaP inverse opals using atomic layer deposition within silica opal templates, confirming fill-hold-purge ALD as ideally suited to uniform film growth within highly porous structures. X-ray diffraction data confirmed the high quality of the GaP. Using this technique, inverse GaP opals were fabricated with filling fractions as high as 0.224, corresponding to 100% of the conformal film growth maximum for an opal lattice. The optical properties of the GaP inverse opal were well described by photonic band calculations, indicating the potential to form a full photonic band gap in the visible. The results demonstrate a reliable, controllable technique for fabrication of inverse opals with a high index, transparent, semiconductor backbone, which avoids anomalous film growth. As GaP is a leading optoelectronic III-V semiconductor, it should be possible to exploit its properties to fabricate active photonic crystal devices with even larger full photonic band gaps using optimized structures.

The authors thank D. P. Gaillot and J. S. King for valuable assistance with this work. This work was supported by the U.S. Army Research Office under MURI Contract No. DAAD19-01-1-0603.

[1] W. Bogaerts, R. Baets, P. Dumon, V. Wiaux, S. Beckx, D. Taillaert, B. Luyssaert, J. Van Campenhout, P. Bienstman, and D. Van Thourhout, J. Lightwave Technol. **23**, 401 (2005).
[2] E. Yablonovitch, Phys. Rev. Lett. **58**, 2059 (1987).
[3] S. John, Phys. Rev. Lett. **58**, 2486 (1987).
[4] S. John and K. Busch, J. Lightwave Technol. **17**, 1931 (1999).
[5] D. Gaillot, T. Yamashita, and C. J. Summers, Phys. Rev. B **72**, 205109 (2005).
[6] A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. López, F. Meseguer, H. Míguez, J. P. Mondla, G. A. Ozin, O. Toader, and H. M. van Driel, Nature (London) **405**, 437 (2000).
[7] E. Palacios-Lidon, A. Blanco, M. Ibisate, F. Meseguer, C. Lopez, and J. Sanchez-Dehesa, Appl. Phys. Lett. **81**, 4925 (2002).
[8] H. Míguez, E. Chomski, F. García-Santamaría, M. Ibisate, S. John, C. López, F. Meseguer, J. P. Mondia, G. A. Ozin, O. Toader, and H. M. v. Driel, Adv. Mater. (Weinheim, Ger.) **13**, 1634 (2001).
[9] Y.-C. Lee, T.-J. Kuo, C.-J. Hsu, Y.-W. Su, and C.-C. Chen, Langmuir **18**, 9942 (2002).
[10] H. M. Yates, M. E. Pemble, E. Palacios-Lidón, F. García-Santamaría, I. Rodriguez, F. Meseguer, and C. López, Adv. Funct. Mater. **15**, 411 (2005).
[11] I. M. Povey, D. Whitehead, K. Thomas, M. E.Pemble, M. Bardosova, and J. Renard, Appl. Phys. Lett. **89**, 104103 (2006).
[12] M. Müller, R. Zentel, T. Maka, S. G. Romanov, and C. M. Sotomayor Torres, Adv. Mater. (Weinheim, Ger.) **12**, 1499 (2000).
[13] B. H. Juárez, M. Ibisate, J. M. Palacios, and C. López, Adv. Mater. (Weinheim, Ger.) **15**, 319 (2003).
[14] E. Palacios-Lidón, H. M. Yates, M. E. Pemble, and C. López, Appl. Phys. B: Lasers Opt. **81**, 205 (2005).
[15] A. Rugge, J. S. Park, R. G. Gordon, and S. H. Tolbert, J. Phys. Chem. B **109**, 3764 (2005).
[16] S. G. Romanov, R. M. D. L. Rue, H. M. Yates, and M. E. Pemble, J. Phys.: Condens. Matter **12**, 339 (2000).
[17] H. M. Yates, W. R. Flavell, M. E. Pemble, N. P. Johnson, S. G. Romanov, and C. M. Sotomayor-Torres, J. Cryst. Growth **170**, 611 (1997).
[18] A. Rugge, J. S. Becker, R. G. Gordon, and S. H. Tolbert, Nano Lett. **3**, 1293 (2003).
[19] J. S. King, C. W. Neff, C. J. Summers, W. Park, S. Blomquist, E. Forsythe, and D. Morton, Appl. Phys. Lett. **83**, 2566 (2003).
[20] J. S. King, E. Graugnard, and C. J. Summers, Adv. Mater. (Weinheim, Ger.) **17**, 1010 (2005).
[21] J. S. King, E. Graugnard, and C. J. Summers, Appl. Phys. Lett. **88**, 081109 (2006).
[22] Y. Sakuma, K. Kodama, and M. Ozeki, Appl. Phys. Lett. **56**, 827 (1990).
[23] M. Ozeki, K. Kodama, Y. Sakuma, N. Ohtsuka, and T. Takanohashi, J. Vac. Sci. Technol. B **8**, 741 (1990).
[24] A. Usui, Proc. IEEE **80**, 1641 (1992).
[25] T. Soga, T. Jimbo, and M. Umeno, J. Cryst. Growth **146**, 554 (1995).
[26] H. Isshiki, Y. Aoyagi, and T. Sugano, Appl. Surf. Sci. **112**, 122 (1997).
[27] N. Y. Li, H. K. Dong, W. S. Wong, and C. W. Tu, J. Cryst. Growth **164**, 112 (1996).
[28] J. S. King, C. W. Neff, S. Blomquist, E. Forsythe, D. Morton, and C. J. Summers, Phys. Status Solidi B **241**, 763 (2004).
[29] S. G. Johnson and J. D. Joannopoulos, Opt. Express **8**, 173 (2001).
[30] D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983). Thin film reflectance measurements were used to independently confirm the index of the ALD grown GaP film.