Photocurable Liquid Core–Fugitive Shell Printing of Optical Waveguides

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Integrated optical systems require waveguides that can route light along defined pathways with minimal losses and negligible crosstalk.[1–3] In addition to signal transmission, optical waveguides play an important role in the area of sensing. For example, evanescent field sensors are applied to the detection of analytes in the body,[4] atmosphere,[5] and liquid solutions.[6] Polymeric and hybrid materials are of increasing interest for these applications due to their low temperature processing.[7] To date, channel waveguides have been fabricated by direct lithographic patterning,[8,9] photoresist-templated etching,[10] or soft-lithographic approaches.[11,12] However, these techniques are limited either to in-plane configurations or require repeated developing or etching steps to produce multiple layers of waveguides. Those processing steps often have a deleterious effect on waveguide performance, leading to rough edges and, hence, higher optical loss.[8,11,13]

Direct-write assembly of optical waveguides is an alternative patterning method, in which soft functional materials are deposited in the desired configuration in a single step. For example, Parker et al.[14] recently patterned silk waveguides by printing a concentrated, viscoelastic ink composed of silk fibroin through a fine deposition nozzle. To maintain its filamentary form, the ink must be deposited into a methanol-rich reservoir to induce rapid coagulation. This approach is not feasible for patterning optical waveguides from photocurable fluids that lack the inherent rheological properties needed for filament formation. Although high-molecular-weight polymers could be added as viscosifying agents, their presence may give rise to inhomogeneities within the printed waveguide that exacerbate optical loss.[15] To overcome this difficulty, fugitive materials have been used as templates to create waveguides from photocurable liquids, but this approach has been limited to simple geometries.[16] To create high-quality waveguides from photocurable liquids, new advances are needed to enable direct filamentary patterning of these soft functional materials.

Here, we report the fabrication of optical waveguides in arbitrary planar and nonplanar configurations via photocurable liquid core–fugitive shell printing (**Figure 1**). Specifically, a hybrid organic–inorganic core fluid, OrmoClear (Micro Resist Technology, GmbH), is encapsulated within a viscoelastic shell composed of an aqueous triblock copolymer, Pluronic F127 (BASF), solution. The fugitive shell serves as a sacrificial support for the core fluid before it is cured with ultraviolet (UV) light. To coextrude these materials in the desired core–shell configuration, a custom printhead was designed and built consisting of two cylindrical nozzles aligned coaxially (see Figure S1 in the Supporting Information). The core fluid and viscoelastic fugitive ink shell are loaded into separate reservoirs and printed simultaneously by applying air pressure to each reservoir. This core–shell geometry produces optical waveguides whose dimensions are dictated by the diameter of the inner nozzle as well as their respective applied deposition pressures.

OrmoClear is of interest for printed waveguides due to its low optical loss in the visible and NIR wavelengths and near-zero shrinkage upon curing, which inhibits crack formation.[17,18] However, OrmoClear is a Newtonian fluid with a viscosity of 5.0 Pa·s and a low shear elastic modulus (G') of 0.35 Pa that is less than its viscous modulus (G'') of 2.5 Pa (**Figure 2**). If this material is deposited alone, it would undergo significant wetting and spreading during waveguide printing. To encapsulate this fluid, we utilize a fugitive hydrogel shell composed of 35 wt% triblock copolymer composed of poly(ethylene oxide), PEO, and poly(propylene oxide), PPO, blocks (Pluronic F127) in deionized water. Note, this material is highly transparent in the visible and ultraviolet wavelengths, allowing for UV-curing of the waveguide core. This fugitive ink was originally developed for printing self-healing materials and hydrogels with embedded 3D biomimetic microvascular networks.[19,20]

Aqueous Pluronic F127 triblock copolymer solutions undergo a phase transition that is both temperature and concentration dependent.[21–23] Pluronic F127 solutions possess a critical micelle temperature (CMT) of ~10 C,[20] in which the PEO–PPO–PEO species form micelles consisting of a PPO core surrounded by a PEO corona. Dehydration of the PPO block leads to pronounced hydrophobic interactions that drive micelle formation. Upon cooling the material below the CMT, the hydrophobic PPO units are hydrated enabling individual PEO–PPO–PEO species to become soluble in water. Under ambient conditions, these solutions exhibit a critical micelle concentration (CMC) of ~21 w/w%. By exploiting their known phase behavior, we have created a stiff fugitive shell composed

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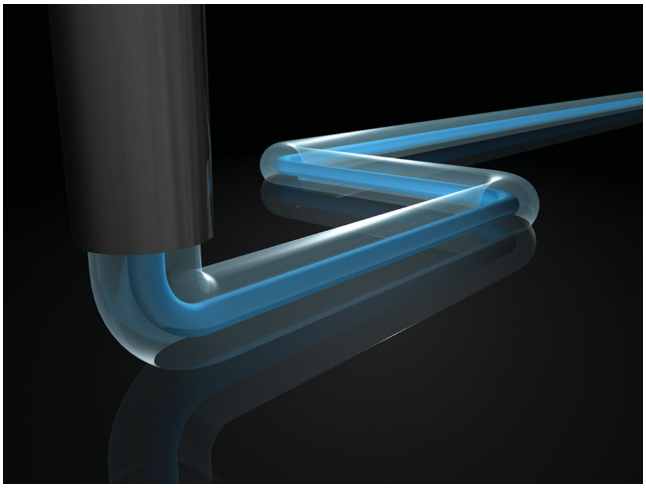

Figure 1. Schematic image of a direct-write assembly of photocurable liquid core–fugitive shell inks for printing polymeric optical waveguides.

of 35 wt% Pluronic F127 in water. This viscoelastic shell exhibits strongly shear thinning behavior with a viscosity that is more than two orders of magnitude higher than OrmoClear at a shear rate of 1 sec^{-1} and a plateau shear elastic modulus of 36 kPa (Figure 2). However, during printing, this shell material flows readily when the applied stress exceeds the shear yield stress of 290 Pa. After the core–shell filamentary architecture exits the printhead, the shell material quickly stiffens as it returns to a quiescent state. Importantly, once the OrmoClear core has been photopolymerized, the Pluronic F127 shell can be liquified and removed by cooling the printed waveguides to ~5 C followed by a water rinse to remove residual Pluronic or by immersing them in deionized water at room temperature. Upon completing the removal process, the patterned waveguides are no longer adhered to the substrate and may be freely (re)positioned.

We first demonstrate liquid core–fugitive shell printing of straight optical waveguides by this approach (**Figure 3**a and Figure S2 in Supporting Information). Despite the low viscosity of the OrmoClear core, the stiff encapsulating shell minimizes spreading and wetting of the printed features. Hence, the waveguide cross-sections remain nearly cylindrical with a cross-sectional width of 431 ± 14 m and a height of 382 ± 19 m (Figure 3a, inset). The observed deviation from a circular cross-section arises because the printed features deform slightly upon contact with the substrate. After printing, the liquid core remains stable within the fugitive shell without leakage for multiple hours and can be photopolymerized by ultraviolet flood exposure. We find that optical waveguides that are cured immediately after printing exhibit a lower optical loss than those left in contact with the fugitive hydrogel shell for several minutes before curing. After 15 min of contact between the uncured core and the shell, an increase inoptical loss from ~0.1 dB cm^{-1} to ~5 dB cm^{-1} is observed (see Figure S3 in the Supporting Information). Diffusion of water from the fugitive shell into the liquid OrmoClear core likely gives rise to the observed deterioration in optical performance.

To minimize optical loss, the printed liquid core–fugitive shell waveguides are cured on-the-fly using a UV light-emitting diode (LED) mounted adjacent to the printhead, similar to methods used previously with single-component inks.[24] The UV LED intensity is systematically varied between 1 and 19 mW cm^{-2}, with higher curing intensity leading to lower optical loss. Specifically, the lowest optical loss observed is approximately 0.1 dB cm^{-1} for printed waveguides cured at an intensity of 19 mW cm^{-2} (Figure 3c). This level of optical loss is comparable to the lowest losses reported for other commercially available, hybrid organic-inorganic materials (i.e., ORMOCERs) patterned in two dimensions by photolithography[25] and superior to those obtained for 3D ORMOCER waveguides patterned by two-photon lithography.[26] Measurements of the waveguide surface by AFM indicate that all printed waveguides produced have a root-mean-square surface roughness between 10 and 20 nm. These values are expected, given that the spherical PEO-PPO-PEO micelles have an average hydrodynamic diameter of 20–80 nm, as reported previously.[21] The low surface roughness values, which are independent of curing intensity, indicate that the core–shell interface is stable and that scattering from the surface of these waveguides does not contribute significantly to their optical loss.

Our approach enables printing of optical waveguides in nearly arbitrary patterns. For example, we have produced OrmoClear waveguides with varying bend radius (Figure 3b). By directly printing curved waveguides, we create features that are stress free, avoiding losses that arise from bending straight waveguides to obtain the desired curvature.[27] Figure 3d shows the optical loss of printed waveguides as a function of radius of curvature (R). Printed waveguides with the sharpest bends of R = 2 mm exhibit the highest optical loss of ~1 dB cm^{-1}, which is expected given that the total internal reflection of transported light is degraded in this geometry. As R increases, the optical loss begins to approach that observed for the straight waveguides. Although there is some scatter in the data, the optical losses ranged from ~0.2–0.5 dB cm^{-1} for printed

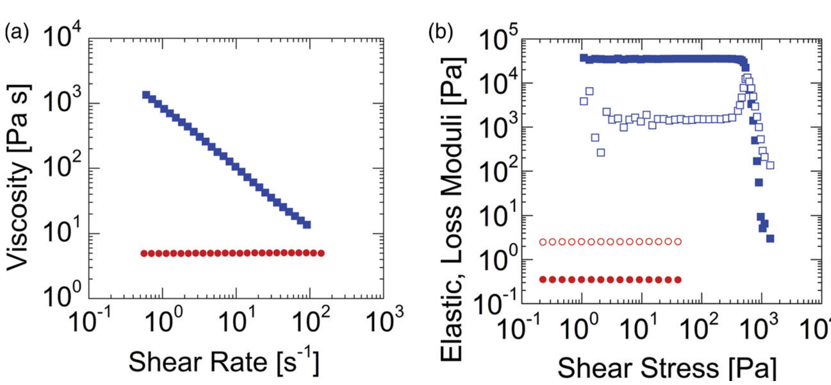

Figure 2. a) Log–log plot of viscosity as a function of shear rate; b) log–log plot of shear elastic (filled symbols) and loss (open symbols) moduli as a function of shear stress for the OrmoClear core (red circles) and aqueous Pluronic F127 (35 wt%) shell (blue squares) materials.

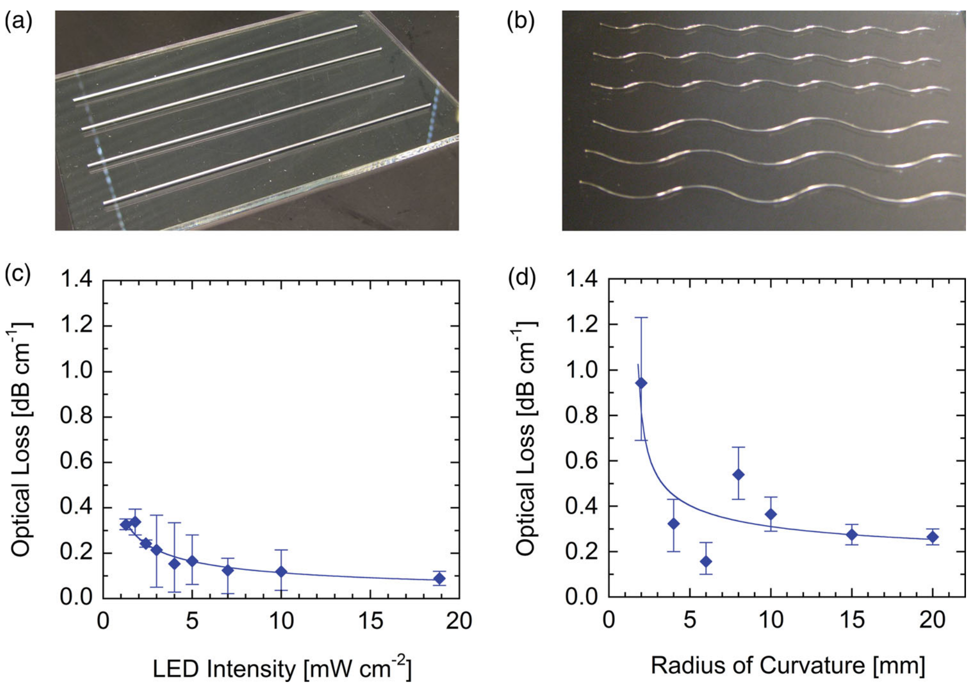

Figure 3. Optical images of (a) straight and (b) curved OrmoClear waveguides; c) optical loss of straight waveguides printed and cured at varying UV LED intensity; d) optical loss of printed curved waveguides cured at a constant LED intensity of 19 mW cm^{-2} as a function of radius of curvature.

waveguides with R = 4–20 mm. Hence, at least a two-fold increase in optical loss is observed for curved waveguides relative to the linear counterparts.

As a final example, we demonstrate the fabrication of an optical waveguide network that carries multiple signals. This network is created by out-of-plane printing of OrmoClear waveguides over other printed planar waveguides that are physically separated at each crossover point due to the presence of their respective fugitive shells. Specifically, we have created a six-waveguide network that is coupled to three different colors of LED light (**Figure 4**). Upon photopolymerization of the OrmoClear liquid cores and removal of the fugitive shells, air gaps are present at each crossover point that enable light to travel through the waveguide network with minimal crosstalk. A higher magnification view of a representative crossover is provided in the Supporting Information (Figure S4). In this example, blue, green, and amber light of respective wavelengths 470, 515, and 590 nm, are each carried through two printed waveguides patterned in either straight (planar) or out-of-plane, curved geometries. The radii of curvature for the in-plane bends are 5 mm, while those associated with the out-of-plane features range from ~3–5 mm. Therefore, optical losses of ~2 db cm^{-1} are expected for light traveling through individual waveguides within this network.

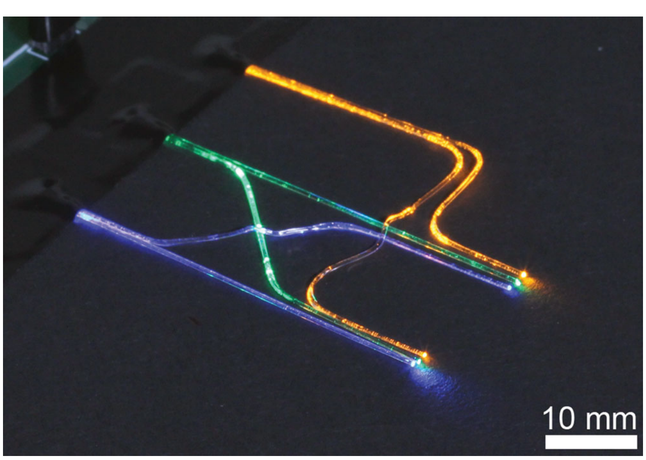

Figure 4. Image of an optical waveguide network composed of six OrmoClear waveguides coupled with three LEDs that distribute colored light with minimal crosstalk.

In summary, we have demonstrated the patterning of hybrid organic–inorganic optical waveguides in straight, curved, and out-of-plane configurations via direct-write assembly of photocurable liquid core–viscoelastic fugitive shell inks. The printed waveguides exhibit nearly cylindrical morphology and low optical loss throughout the visible spectrum. Their fugitive shells enable printing of optical waveguide networks coupled to multiple LEDs, with gaps at the crossover points between waveguides to reduce crosstalk. Our approach offers a flexible method for producing waveguide networks for integration with high-bandwidth next-generation optical systems and optical sensor arrays.

Experimental Section

Materials System: The photocurable liquid core is composed of OrmoClear (Micro Resist Technology), which is available commercially and used as-received. The viscoelastic fugitive ink shell is prepared by adding 35 wt% of a triblock copolymer composed of hydrophilic poly(ethylene oxide), PEO, and hydrophobic poly(propylene oxide), PPO, blocks in a PEO-PPO-PEO configuration, with an average molecular weight of 12 kDa and 70 wt% PEO (Pluronic F127, BASF) to deionized water. The solution was mixed mechanically for 2 h in an ice-water bath to disperse the Pluronic, then refrigerated for 48 h at 4 C to defoam. This solution is then poured into the printing reservoir and equilibrated at room temperature before use. Above 20 C, this solution undergoes a transition from a liquid to a viscoelastic gel due to the hydrophobic interactions between PPO segments that drive micelle formation.

Ink Rheology: The rheological properties of the OrmoClear and Pluronic F-127 are measured using a controlled-stress rheometer (CVOR-200, Bohlin). A cone and plate geometry is used for OrmoClear, and a cup and bob geometry is used for Pluronic F-127, which is loaded into the cup as a fluid at ~5 C The temperature of these materials is held at 22 C by a circulating water bath (Model 9110, Polyscience). The ink viscosity is measured under steady-state shear, while the shear elastic and viscous moduli are measured in oscillatory mode, at a frequency of 1 Hz, in which the stress amplitude is incrementally increased.

Core–Shell Printhead: The core–shell printhead is constructed from stainless steel tubing (McMaster Carr, Inc), which is cut to length and polished. The shell tubing (I.D. 1270 m, O.D. 1470 m) is placed in a custom alignment jig and then the core tubing (I.D. 355 m, O.D. 560 m) is inserted into it. Proper coaxial alignment of the core tubing is achieved manually and the two lengths of tubing were fastened in place with Norland Optical Adhesive 63 (Norland Products). Luer-lock inputs (EFD Inc) are connected to the core and shell tubing and sealed in place with two-part epoxy. For the targeted application, waveguides with diameters of approximately 400–800 m are desired, which can be achieved using this printhead at varying applied pressures.

Waveguide Fabrication: The OrmoClear and hydrogel materials are loaded into syringe barrels (diameter = 15.8 mm, EFD Inc) and attached to two input locations on the core–shell printhead, which is mounted on the *x–y–z* positioning stage (Aerotech, Inc). The core and shell inks were extruded under applied air pressure (Ultimus V dispensing system, EFD Inc) of 482 kPa and 345 kPa, respectively, at a deposition speed of 10 mm s^{-1}. The separation of the tip of the printhead and the glass substrate is maintained at 1.6 mm during waveguide printing. To prevent leakage, sealed ends are created by applying pressure to the shell ink prior to the core ink, and removing pressure from the core ink prior to the shell ink at the beginning and end of each waveguide structure.

Waveguide Curing: Waveguides were cured on-the-fly by exposure from a UV LED (NCSU033A, Nichia) mounted adjacent to the printhead. The LED is positioned approximately 15 mm behind the printhead tip and 20 mm above the waveguide during printing. The LED intensity is controlled by custom pulse-width modulation circuitry to deliver 1–20 mW cm^{-2} of intensity at 365 nm.

Waveguide Characterization: After fabrication, waveguides are tested for optical throughput using the cutback method. A Helium–Neon laser (155 SL, Uniphase) operating at 633 nm is aligned with one end of the sample and output from the other end is measured using a photodetector (808-LL, Newport). The measured current from the detector is converted to dB. After each measurement, the waveguide is carefully cut-back in length by approximately 1 cm and the output is measured again. From these data, we determined a linear relationship between output, measured in dB, and sample length, from which the light loss, in dB cm^{-1} is extracted. The reported data are average values obtained from measuring 2–4 waveguides per data point, and the error bars shown correspond to the minimum and maximum values obtained.

Waveguide/LED Networks: Surface-mount, right-angle LEDs with blue, green, and amber (APA1606QBC/D, APA1606ZGC, and APA1606SYCK, Kingbright Elec. Co.) peak wavelengths of 470, 515, and 590 nm are mounted at the edge of a custom-designed printed circuit board. These LEDs have an output lens with height 0.6 mm and width 1.6 mm oriented horizontally. Printed waveguides with the desired geometry are positioned such that their ends are flush to the output lens of each LED. Two waveguides are matched to each LED and their ends are positioned side-by-side. The LEDs and waveguide-ends are covered with black insulating tape to hold them in position and eliminate the portion of light not coupled into the waveguides. The LEDs are powered by an input voltage of 5 V DC, and their apparent brightnesses are matched by adjusting an inline potentiometer between 100–1100 Ω.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[1] M. Law, *Science* **2004**, *305*, 1269.
[2] R. T. Chen, L. Lin, C. Choi, Y. J. Liu, B. Bihari, L. Wu, S. Tang, R. Wickman, B. Picor, M. K. Hibb-Brenner, J. Bristow, Y. S. Liu, *Proc. IEEE* **2000**, *88*, 780.
[3] N. M. Jokerst, M. A. Brooke, Sang-Yeon Cho, S. Wilkinson, M. Vrazel, S. Fike, J. Tabler, Yoong Joon Joo, Sang-Woo Seo, D. S. Wills, A. Brown, *IEEE J. Sel. Top. Quant.* **2003**, *9*, 350.
[4] S. W. Kwon, W. S. Yang, H. M. Lee, W. K. Kim, G. S. Son, D. H. Yoon, S. D. Lee, H. Y. Lee, *Appl. Surf. Sci.* **2009**, *255*, 5466.
[5] D. J. Sirbuly, S. E. Létant, T. V. Ratto, *Adv. Mater.* **2008**, *20*, 4724.
[6] A. Prabhakar, S. Mukherji, *Lab Chip* **2010**, *10*, 748.
[7] H. Ma, A. K. Y. Jen, L. R. Dalton, *Adv. Mater.* **2002**, *14*, 1339.
[8] U. Streppel, P. Dannberg, C. Wächter, A. Bräuer, L. Fröhlich, R. Houbertz, M. Popall, *Opt. Mater.* **2003**, *21*, 475.
[9] S.-H. Nam, J.-W. Kang, J.-J. Kim, *Macromol. Res.* **2006**, *14*, 114.
[10] T. Kaino, B. Cai, K. Takayama, *Adv. Funct. Mater.* **2002**, *12*, 599.
[11] L. Wang, X. Wang, W. Jiang, J. Choi, H. Bi, R. Chen, *Appl. Phys. Lett.* **2005**, *87*, 141110.
[12] X. Dou, X. Wang, H. Huang, X. Lin, D. Z. Pan, R. T. Chen, *Optics Express* **2010**, *18*, 378.
[13] Y. Liu, L. Lin, C. Choi, B. Bihari, R. T. Chen, *IEEE Photonics Technol. Lett.* **2001**, *13*, 355.
[14] S. T. Parker, P. Domachuk, J. Amsden, J. Bressner, J. A. Lewis, D. L. Kaplan, F. G. Omenetto, *Adv. Mater.* **2009**, *21*, 2411.
[15] A. Yeniay, R. Gao, *Appl. Optics* **2010**, *49*, 3684.
[16] M. Hajj-Hassan, T. Gonzalez, E. Ghafar-Zadeh, H. Djeghelian, V. Chodavarapu, M. Andrews, D. Therriault, *Sensors* **2008**, *8*, 7636.
[17] S. Uhlig, L. Frohlich, M. Chen, N. Arndt-Staufenbiel, G. Lang, H. Schroder, R. Houbertz, M. Popall, M. Robertsson, *IEEE Trans. Adv. Packag.* **2006**, *29*, 158.
[18] G. Schmid, W. Leeb, G. Langer, V. Schmidt, R. Houbertz, *Electron. Lett.* **2009**, *45*, 219.
[19] C. J. Hansen, W. Wu, K. S. Toohey, N. R. Sottos, S. R. White, J. A. Lewis, *Adv. Mater.* **2009**, *21*, 4143.
[20] W. Wu, A. DeConinck, J. A. Lewis, *Adv. Mater.* **2011**, *23*, H173.
[21] M. Bohorquez, C. Koch, T. Trygstad, N. Pandit, *J. Colloid Interface Sci.* **1999**, *216*, 34.
[22] P. Linse, M. Malmsten, *Macromolecules* **1992**, *25*, 5434.
[23] G.-E. Yu, Y. Deng, S. Dalton, Q.-G. Wang, D. Attwood, C. Price, C. Booth, *J. Chem Soc.-Faraday Trans.* **1992**, *88*, 2537.
[24] L. L. Lebel, B. Aissa, M. A. E. Khakani, D. Therriault, *Adv. Mater.* **2010**, *22*, 592.
[25] K. Yoon, *Macromol. Res.* **2004**, *12*, 290.
[26] V. Schmidt, L. Kuna, V. Satzinger, R. Houbertz, G. Jakopic, G. Leising, *Proc. SPIE.* **2007**, *6476*, 64760P.
[27] Y. C. Chen, *Appl. Optics.* **2007**, *46*, 4570.