

## Photoimageable, Low Shrinkage Organic–Inorganic Hybrid Materials for Practical Multimode Channel Waveguides

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Optical waveguides have been a subject of interest over the past decade because they offer great promise for applications as optical interconnects used in telecommunication networks, local- and wide-area networks (LAN and WAN), sensors, and other optoelectronic devices.<sup>1,2</sup> Both organic and inorganic materials have been used to fabricate such optical interconnection devices. Organic polymers offer ease of processibility and toughness, and inorganic materials offer superior thermal resistance and compatibility with common inorganic substrates. Recently, organic–inorganic hybrid materials have been increasingly studied as waveguide materials<sup>3–7</sup> because, as a new class of materials between traditional organic and inorganic materials, they offer promising properties that are not readily available from conventional organic or inorganic materials.<sup>8</sup> So far, however, fabrication of economically viable waveguide devices from such hybrid materials has not been very successful.

One of the difficulties lies in the severe volume shrinkage (more than 50%)<sup>9</sup> that accompanies the curing of sol–gel materials, leading to cracking. This shrinkage problem not only limits the film thickness to below 1  $\mu\text{m}$  for pure inorganic sol–gel materials and 10  $\mu\text{m}$  for the hybrid materials but also requires impractical curing and drying times (often several weeks or even months) to obtain a homogeneous, monolithic structure. The other problem is phase

separation, especially upon prolonged use, which increases optical scattering loss. A further difficulty is that most sol–gel systems cannot be photoimaged because of low photolithographic sensitivity and/or contrast. Constrained by these problems, the sol–gel waveguides reported so far have been very thin (<10  $\mu\text{m}$ ) and have been mostly fabricated as slab-type waveguides. For practical optical interconnection applications, however, channel waveguides whose refractive index, cross-sectional dimensions and numerical aperture (NA) match those of commercial optical fibers are preferred to reduce connection loss. Schmidt<sup>4</sup> and Prasad<sup>7</sup> and their co-workers have recently reported fabrication of thin hybrid channel waveguides with optical propagation loss smaller than 1.0 dB/cm by laser writing and local laser-densification techniques, respectively.

Very recently, exciting progress in the field of sol–gel hybrid materials has been made by Novak<sup>10</sup> and Wei<sup>11</sup> and their co-workers in preparation of low-shrinkage sol–gel hybrid materials. Their low shrinkage methods allow for fabrication of large-dimension objects without cracking within a reasonable period of time. In the optical interconnect area, we have made significant advances in developing high-performance optical devices and a novel approach to couple optical fibers with low loss and low cost (i.e., flexible polymer gripper technology).<sup>12</sup> By exploiting the new low-shrinkage sol–gel technologies and our recent advances in high contrast and low-loss polymeric waveguiding materials, we have designed and synthesized a system of photoimageable, low-shrinkage, organic–inorganic hybrid materials. From these materials, low loss multimode channel waveguides that match multimode glass fibers in both NA and cross section have been fabricated by photolithography.

The scheme of this work involves two basic concepts. One is to covalently attach well-known photocurable acrylate moieties to the inorganic sol–gel precursor polymer so that high-contrast channel waveguide structures can be defined from the hybrid materials and fixed through photoimaging of the organic groups. To achieve this goal, an organic–inorganic phase coupling agent, such as (3-acryloxypropyl)methyldimethoxysilane (AMDS), is used to introduce acrylate groups to the silica prepolymer. Photocuring of the mixture of the acrylate containing silica prepolymer and other acrylate monomers yields an organic–inorganic covalently interconnected hybrid network, which prevents phase separation into domains large enough to cause light scattering. The condensation of the sol–gel process can be furthered by postbaking. The second concept, which is employed together with the first, is to achieve low shrinkage hybrid materials by using a solvent-free approach so that thick films and hence large cross-section multimode devices can be fabricated to match

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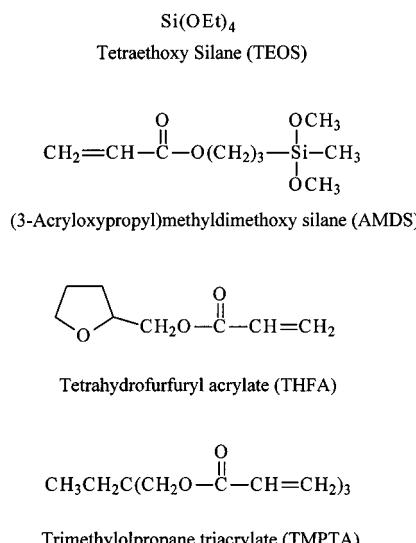
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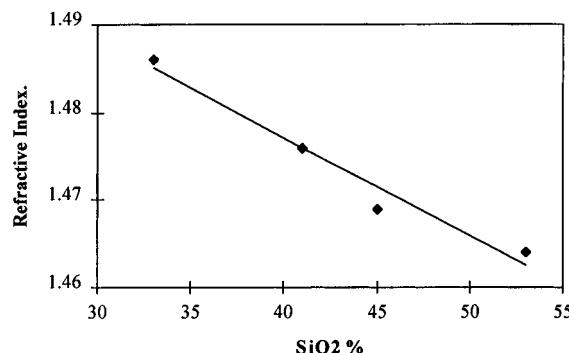


**Figure 1.** Structures of monomers used in the hybrid materials

commercial glass optical fiber cores in size, which are typically 50–100  $\mu\text{m}$  in diameter, for low loss connection.

Figure 1 lists the structures of the monomers used in the hybrid polymer system. The silica prepolymer with pendant acrylate groups and its mixture with other acrylate monomers was prepared by refluxing a tetrahydrofuran (THF) solution containing tetraethoxysilane (TEOS), AMDS, tetrahydrofurfuryl acrylate (THFA), trimethylolpropane triacrylate (TMPTA), dilute hydrochloric acid aqueous solution (HCl), and 1,1-dimethoxy-1-phenylacetophenone (I-651). Among the ingredients, TEOS is a precursor monomer, which, after hydrolysis and subsequent condensation, forms a silica network; AMDS is the organic–inorganic phase coupling agent, which can react with both organic and inorganic monomers and provides covalent linkages between the organic and inorganic networks; THFA acts as nonvolatile, photocurable solvent, which is used to adjust viscosity and increase the shelf life of the prepolymer mixture; TMPTA is a multifunctional acrylate monomer and acts as a cross-linker for the organic phase; HCl is the catalyst for the sol–gel process; I-651 is a free radical photoinitiator for UV curing; and THF is the reaction solvent. After 1.5 h of refluxing to fully hydrolyze the alkoxy silanes and partially condensate the resulting hydroxysilanes, the mixture was cooled to room temperature. The volatile solvent THF and byproducts including alcohols and water as well as residual HCl were removed by vacuum evacuation to yield a colorless, viscous liquid. The liquid can be molded into bulky objects or cast into films, which can then be cured by UV exposure followed by postbaking. The inorganic content (SiO<sub>2</sub>% by weight) was varied from 30 to 60% by formulation and determined by TGA. After the films were heated to 800 °C under air atmosphere with a TGA analyzer, they turned from colorless and clear to white and nontransparent but maintained their shape. The residual weight of the white films was taken as the inorganic content, SiO<sub>2</sub>%.

To determine volume shrinkage, a small cylinder of 1 cm diameter was molded by curing and postbaking the hybrid liquid in a glass vial. The volume shrinkage was measured to be between 10 and 20%, depending

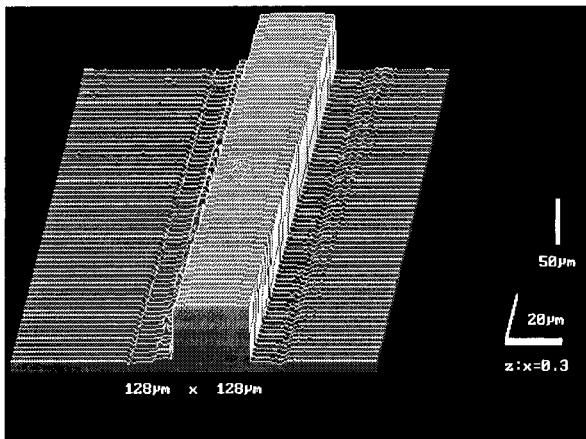


**Figure 2.** Refractive indexes of the hybrid materials as a function of SiO<sub>2</sub>%.

on the SiO<sub>2</sub>%. This range is significantly lower than conventional sol–gel materials, for which shrinkage can be as high as 75%.<sup>9</sup> This low shrinkage is attributed to the removal of volatile solvent and byproducts before photocuring. Films as thick as 0.5 mm have been prepared by photocuring and postbaking. It was found that for high SiO<sub>2</sub>% materials, rapid heating caused the thick films to crack, indicating stress and material brittleness. Gradual, multistage postbaking, on the other hand, resulted in integral 0.5 mm thick films as large as 100 cm<sup>2</sup>.

For optical interconnection applications, the waveguiding materials must be of low optical loss including low absorption, low scattering, and low reflection at the waveguide–optical fiber interface. The hybrid materials synthesized are all colorless and have low intrinsic absorption in the wavelength range 400–900 nm. The organic–inorganic phase coupling agent used in the system prevents phase separation and hence reduces scattering loss. To minimize the reflection loss at the waveguide–fiber interface, silica has been chosen as the inorganic phase to reduce the refractive index difference with glass fibers. For waveguide materials, it is also important to have the capability to tailor the refractive index so that the index difference between the core and cladding layers can be controlled. This index difference determines the modal characteristics and NA of a waveguiding device. The refractive indexes ranging from 1.46 to 1.49 of our hybrid materials were tuned by varying the SiO<sub>2</sub>%. Figure 2 illustrates the relationship between the refractive index and the SiO<sub>2</sub> weight percentage. The refractive index, which was measured at 633 nm wavelength, decreases linearly with increasing the SiO<sub>2</sub> weight percentage, within our experimental range. This linear relationship allows us to precisely tailor the refractive index of the hybrid materials and therefore the NA of the waveguides. In fact, we have fabricated several waveguides using the high-index composition (low SiO<sub>2</sub>%) as the core and the low-index (high SiO<sub>2</sub>%) composition as the cladding with controlled refractive index difference and NA.

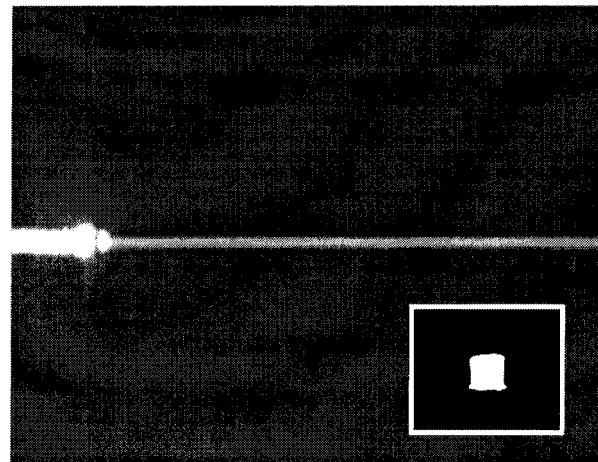
The waveguide devices were fabricated by conventional photolithographic techniques. The viscous liquid obtained was filtered through a 0.1  $\mu\text{m}$  syringe filter before use to remove foreign particulates. A low-index layer was first coated onto a silicon wafer and photocured to serve as the cladding. A higher index layer of liquid was spread on the cladding layer as the core. A photomask was then placed on top of the core layer. The thickness of the core layer was controlled by spacers placed between the substrate and the mask as well as



**Figure 3.** LSM picture of a multimode channel waveguide written from the hybrid materials by photolithography.

the pressure applied. The core material was cured by about 100 mJ of UV exposure through the mask features. After removal of the photomask, the image-wise waveguide structures were developed using methanol. The defined structures were subsequently post-baked at temperatures below 80 °C. Figure 3 shows a confocal laser scanning microscope (LSM) picture of a channel waveguide. Well-defined structures with smooth and vertical walls have been obtained, indicating the very high photocontrast for the hybrid materials. The high photocontrast is very important as it permits control of device geometry and allows for fabrication of high-density waveguide arrays for complex structures. The smooth wall surface is also desirable for low scattering loss. Due to the low shrinkage and solvent-free nature of the materials, thick films and therefore large-dimension devices have been produced. The capability to produce thick structures without cracking enables us to fabricate multimode waveguides that match commercial multimode glass optical fibers with diameters ranging from 50 to 100  $\mu$ m. The NA's of the waveguides fabricated, ranging from 0.19 to 0.29, were controlled by selecting the cladding and core materials with appropriate refractive index differences.

Figure 4 shows the CCD camera frame-grabbed picture of the input end of a channel waveguide irradiated by an 810 nm laser. No scattering from localized defects was observed along the 5 cm guide, which



**Figure 4.** CCD camera frame grabbed picture of a channel waveguide irradiated by an 810 nm laser.

demonstrated a highly homogeneous and uniform structure. The output intensity profile of the guide is virtually square and simply reflects the shape of the waveguide cross section. Optical propagation loss of 0.27 dB/cm was determined by measuring the intensity of the scattered light as a function of the propagation path length.

In conclusion, we have developed a system of photo-imageable, low-shrinkage hybrids of acrylate polymers and silica. Covalent attachment of acrylate moieties to the sol–gel silica precursor through an organic–inorganic phase coupling agent allows for fabrication of uniform, well-defined channel waveguides by conventional photolithography techniques. Removal of volatile solvent and byproducts before photocuring and post-baking resulted in very low shrinkage materials. By taking advantage of the materials high contrast and low shrinkage as well as tailorabile refractive index, well-defined multimode channel waveguides have been successfully fabricated that match both the cross-sectional dimensions and the numerical aperture of multimode glass optical fibers. Due to the excellent homogeneity of the cured hybrid materials and the smooth walls of the devices, a low propagation loss has been realized with the hybrid waveguides.

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