Selective-area doping of porous solgel films for integrated optics

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A technique for doping of porous films by surface adsorption of ions from aqueous solution is demonstrated. Fabrication of the films by use of the solgel technique gives a nanometer-scale porosity, which provides high doping levels and homogeneity. Doping through a masking layer patterned by photolithography is thus possible. With Pb as a dopant, lead silicate films with refractive indices of 1.46 to 1.55 were obtained, with submicrometer patterning resolution. Linear control of the refractive index is achieved through variation of the solution pH. Applications of this technique in integrated optics and optical elements are proposed.

The formation of channel waveguides for integrated optics (IO) requires patterning of the waveguiding material with high resolution. In both semiconductor and silica-on-silicon IO technologies, topographic techniques are usually employed. The silica-on-silicon process based on flame hydrolysis deposition (FHD), is a typical example. A glass buffer layer is deposited, followed by a guiding layer of higher refractive index. The waveguiding pattern is defined by conventional photolithography and transferred to the guiding layer by reactive ion etching. Finally, the guiding ridges are buried by a further low-index cladding layer. The remaining surface relief is not ideal for further lithography steps, and such techniques are not well suited to the formation of directly adjacent regions of different composition.

An alternative approach is to modify the index locally by use of a patterned doping technique. A dopant can be introduced by thermal diffusion, although this is slow and requires high temperatures. Ion exchange provides large index differences and requires more modest temperatures but is possible only with a quite limited range of compositions.

Besides the formation of waveguides, doping of glasses for IO may be desired for the introduction of species that are not easily introduced into the glass fabrication or deposition method itself. Solution doping of films made by FHD with rare-earth ions has been studied; however, because the particles created by FHD are on the micrometer scale, high consolidation temperatures are required for homogeneous glass, whether solution doping has been employed or not.

In the solgel technique oxide particles are formed by the hydrolysis and polycondensation of metal alkoxides as a colloidal suspension (the sol). Drying of the sol after casting or film deposition results in gel formation by further condensation, and heat treatment of this gel will remove residual organics to give an inorganic glass. Unless reflow temperatures are reached during this process, the resulting glass in porous, and for an acid-catalyzed sol this porosity can be on a nanometer scale. Such porous glasses provide a useful host for various doping techniques and can give high homogeneity of the end product without further treatment at melt or near-melt temperatures.

Rabinovitch et al. fabricated multicomponent glasses by impregnating dried gel monoliths with aqueous solutions of various metal salts. However, to avoid the cracks that tend to result in the drying of structures with nanometer pores because of the very large attendant capillary stresses, Rabinovich et al. formed larger pores (~10–100 nm) by combining acid and alkaline catalysis. As in the FHD case the dopant precursor was essentially precipitated in the structure. Kondo et al. doped porous gels by adsorption of vapor phase dopants such as GeCl₄ within the pores. Impregnation of solgel materials with photosensitive organics, allowing subsequent patterning by direct UV exposure, was reported by Mendoza et al. Here we demonstrate doping of nanoporous films from aqueous solutions, where adsorption on the internal surface rather than precipitation is the doping mechanism.

We have demonstrated a technique for characterizing the nanoporosity of solgel films and determined process parameters for maximizing the porosity. These parameters were used as the starting point for this study. The fractional porosity of ~20% in solgel films consists mainly of pores less than 1 nm in diameter. This scale means that the porous films are effectively uniform, solid, and smooth for the purposes of lithography, and the large internal surface areas allow high doping levels to be achieved.

All sols were prepared with equal volumes of tetraethyl orthosilicate and ethanol, mixed with 0.1-M HCl to a molar ratio (water to tetraethyl orthosilicate) of $R = 2$, and then refluxed for 2 h at 70 °C. We fabricated films by dispensing the sol onto a silicon wafer and spinning it at 3000 rpm for 30 s. The films were then baked in a tube furnace at a temperature that we call the prebake temperature. Film thicknesses were typically 500 nm.

Patterning was done with standard photolithographic procedures by use of Microposit S1400-27 photoresist. After resist coating, samples were baked for 30 min at 90 °C before exposure (by direct contact)
and development (with Microposit MF-319 developer). A hard bake at 110 °C was carried out within 2 h of doping.

We prepared doping solutions with a molarity of 0.05 M by dissolving lead acetate trihydrate in deionized water. The pH of the solution was measured with an Oyster pH meter and adjusted with acetic acid and ammonia as required. We doped the samples by soaking them in this solution for 30 min at room temperature and then rinsing them thoroughly in deionized water. The resist was removed by an acetone rinse, followed by a further rinse in deionized water. Finally the films were baked in a tube furnace until they were fully densified, as indicated by their reaching a maximum refractive index. The required temperature was typically in the range 700±1000 °C, depending on the amount of lead present; we call this the postbake temperature. The complete process is illustrated in Fig. 1.

The porosity of films before doping was estimated with ellipsometry by measurement of the refractive index under both dry and water-saturated N₂ and use of the Lorenz–Lorentz equation to calculate the skeleton index and volume fraction porosity. The refractive indices after doping and densification were used as a relative measure of the amount of lead adsorbed. By assuming that the dopant after densification is in the form of PbO, as indicated by UV–visible absorption spectra, we can relate the index to the composition by extrapolating the data of Ref. 10. The presence and quantity of Pb in the films were also measured by electron energy-dispersion spectrometry. Fourier-transform infrared spectra were taken at various stages of the process. Within the spectral range used (400–4000 cm⁻¹) the Pb–O bond, which occurs at 135 cm⁻¹, could not be monitored; however, the results indicated that no organic contaminants were introduced by the photolithographic process and confirmed that the densification temperatures coincided with the removal of residual hydroxyls.

An example of selective-area doping is shown in Fig. 2. A mask with gratings of different pitches was used, the minimum of which had a linewidth of 2 μm. The left-hand side of the picture shows the undoped region of pure silica (index, 1.46), and the darker lines on the right-hand side show the Pb-doped area, with index 1.50. The selectivity of doping is clearly demonstrated, and submicrometer edge definition is obtained, which is sufficient resolution for single-mode channel waveguides.

We carried out experiments on unpatterned samples to investigate mechanisms for controlling the amount of adsorption. First the porosity of the silica films was varied through the prebake temperature. The results are shown in Fig. 3. As expected, the porosity increases to a maximum at approximately 400–500 °C, at which the remaining organics are burned off, and then decreases with temperature until full densification is reached at ~1000 °C. A strong correlation between porosity and index can be seen. However, the nonlinearity of the dependence on temperature suggests this is not an ideal parameter for control of the doping level.

An alternative approach is to control the reaction chemistry. This was done by control of the pH of the doping solution. According to Schindler et al., adsorption can be expected to follow a characteristic
s-shaped curve, with a sharp increase over the pH range from 4.5 to 6.5. We found that doping at a pH level of less than 5.2 gave no measurable adsorption, whereas with a pH of more than 6.4 precipitation of lead hydroxide caused poor surface quality.

We fabricated the samples as described above, pre-baking them at 500°C for 30 min. The results, shown in Fig. 4, indicate a linear relation between doping level and pH. The highest index of 1.55 suggests a level of ~30-wt. % PbO. We repeated the experiment to check the reliability of the process; the two sols used were made according to the same process, and the slight difference in doping level that was seen is within experimental error.

In conclusion, a method has been developed for selective-area doping of porous silica films that yields glass films of patterned composition with high resolution. Unlike techniques that involve precipitation of dopants within pores, this method is based on surface adsorption, which allows removal of any deposits from the external surface without loss of internal dopants. Because of the high internal surface area, high doping levels are achieved, allowing a wide range of refractive index to be obtained. One can achieve accurate control by doping the solution pH. The final product is a fully inorganic glass, offering the possibility of high transparency at telecommunications wavelengths. The technique is rapid, and the densification process temperatures are relatively low.

We believe that the technique presented here is applicable to a wide range of dopants. The introduction of rare-earth ions is one possible application, and patterned rare-earth doping could allow monolithic integration of amplifying and passive glass IO functions. For IO in general, further research is needed for fabrication of doped films of greater thickness and demonstration of channel waveguides. Applications in other areas, for example, in the fabrication of diffractive optical elements, for which the large index variation attainable and the wide transparency range of silica-based glasses will be beneficial, may also be possible.

References