

Soft lithography molding of polymer integrated optical devices: Reduction of the background residue

George T. Palocz, ^{a)} Yanyi Huang, Jacob Scheuer, and Amnon Yariv
Department of Applied Physics, California Institute of Technology, Mail Code 128-95, Pasadena, California 91125

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Soft lithography molding is a promising technique for patterning polymer integrated optical devices, however the presence of a background residue has the potential to limit the usefulness of this technique. We present the soft lithography technique for fabricating polymer waveguides. Several effects of the background residue are investigated numerically, including the modal properties of an individual waveguide, the coupling ratio of a directional coupler, and the radiation loss in a waveguide bend. Experimentally, the residue is found to be reduced through dilution of the core polymer solution. We find that the force with which the soft mold is depressed on the substrate does not appreciably affect the waveguide thickness or the residue thickness. Optical microscope images show that the residue is thinnest next to the waveguide. © 2004 American Vacuum Society.
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I. INTRODUCTION

Polymers are fast becoming important materials for optoelectronics. Significant examples include mechanically flexible “electronic paper”¹ and high efficiency light-emitting diodes based on electroluminescent conjugated polymers.² A similar promise is being presented for polymers in telecommunications-related integrated optical devices due to several favorable material features.³ As required by the application, polymer materials can be made functional in several ways. Polymers not intrinsically functional can be doped with numerous optically active dopants such as organic laser dyes,⁴ rare-earth light-amplifying complexes,⁵ and electro-optic dyes.⁶ The “soft” nature of the materials differs from crystalline materials, enabling flexible free-standing electro-optic modulators⁷ and filters.⁸ The low material costs are a basic consideration for mass production of polymer optoelectronic devices. In contrast to semiconductor materials that require several successive growths to make the raw material, polymer waveguide and cladding layers are simply sequentially spun onto a rigid substrate. Thus far, the fabrication techniques for integrated optical devices have been mostly limited to standard semiconductor fabrication techniques such as ultraviolet (UV) or electron beam lithography, reactive ion etching, and wet etching. Fabrication techniques that reduce both the cost and time required for fabricating integrated optical components must be employed to fully take advantage of the intrinsic properties of polymers.

Soft lithography has proven to be a powerful technique for fabricating many structures.⁹ Optical devices made by soft lithography have been mostly limited to the visible regime. The process is, however, largely unexplored for producing complex polymer optical elements useful for infrared telecommunications applications. Implemented by Zhao *et al.* to make polymer optical couplers¹⁰ in the visible regime, the technique has been extended to make polymer dis-

tributed feedback and distributed Bragg reflector lasers,⁴ hybrid organic/inorganic photonic crystal lasers,¹¹ and mesoporous silica waveguide lasers.¹² It has been recently shown that soft lithography is amenable to producing integrated optical components in the infrared regime, such as optical interconnects¹³ and microring optical filters.¹⁴ The latter work particularly demonstrates the high fidelity and precision required to achieve the performance needed for fabrication of devices in the telecommunications component industry. In contrast, hard-mold replication, or hot embossing, of polymer devices has been used to make several devices, for example microring resonators,¹⁵ but this technique presents several difficulties. For complex, multilayer devices this procedure is less useful due to the high temperatures needed to reflow the polymer film. The high temperatures needed for reflow could disturb lower cladding layers and possibly alter optically active dopant molecules. Furthermore, this process is also of limited use for cross-linking polymer films because for these materials, the degradation, and glassy temperatures occur at nearly the same temperature. Finally, hard molding is less useful for mass production due to pattern defects caused by the physical contact between the mold and the substrate, thus limiting multiple use of the hard mold.

In this article, we present the soft-mold replication technique for fabrication of polymer optical waveguide devices. The technique has been well studied for making nanoscale features,⁹ and has proven to have sufficient resolution for making integrated optical components,¹⁴ with feature sizes down to tens of nanometers.¹⁶ However, a limiting difficulty of this technique remains. The ubiquitous presence of a background residue of polymer material has the potential to ruin the desired optical performance of devices. We study numerically the impact of the presence of the residue on simple optical waveguides, on the coupling output ratio of directional couplers, and on the radiation losses in waveguide bends. We investigate techniques of reducing the residue to

^{a)}Electronic mail: palocz@caltech.edu

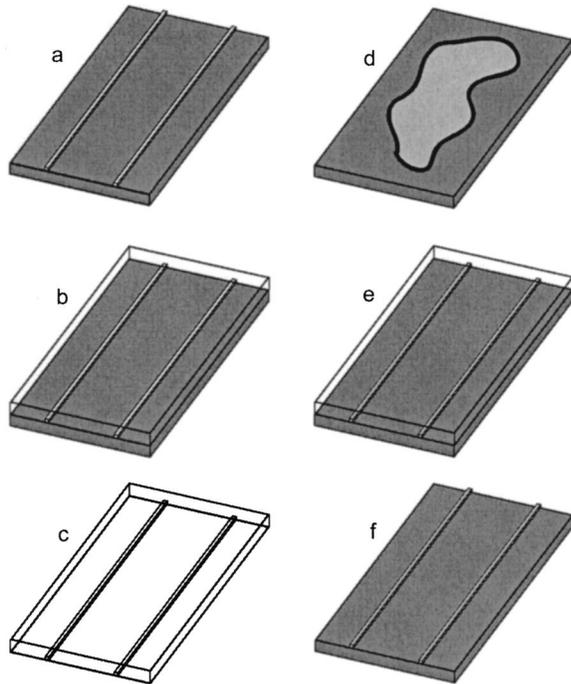


FIG. 1. Schematic diagram of the replica molding process for polymer waveguide devices. (a) The master device is fabricated in SU-8 resist by UV or electron-beam exposure. (b) PDMS is poured atop the master device and thermally cured. (c) Once cured, the PDMS mold is peeled from the master device. (d) A drop of the core polymer solution is placed on an appropriate substrate. (e) The PDMS mold is depressed. (f) Once cured, the PDMS mold is peeled to expose the molded replica.

acceptable levels. Control of the residue to acceptable levels leads the way to the mass production and deployment of polymer integrated optical devices fabricated by soft-mold replication.

II. EXPERIMENTAL PROCEDURE

The process-flow diagram is shown in Fig. 1. The master device is first prepared by photolithographic patterning of SU-8 resist on a bare silicon substrate [Fig. 1(a)]. The master is baked for 1 h at 150 °C to harden the structures and to smooth out nanometer scale sidewall and surface imperfections due to the exposure and developing. To make the mold, liquid poly (dimethylsiloxane) (PDMS) is poured atop the master device in a Petri dish [Fig. 1(b)]. The PDMS is cured for 1 h at 80 °C, upon which the mold is peeled from the master device [Fig. 1(c)]. The mold is approximately 0.5 cm thick and is diced to a size of 1.8×3.8 cm in width and length, respectively.

To make the replica device, a drop of solution is placed on an appropriate substrate [Fig. 1(d)], and the mold is depressed [Fig. 1(e)]. To guide light, the substrate must have a layer of material with a lower refractive index than the core light-guiding material. Typically a layer of SiO₂ ($n = 1.45$) or another polymer ($n = \sim 1.3 - 1.6$) is used. Here, for the investigation of the effects of molding parameters on the structural features, we use bare silicon as the substrate. The core polymer solution is prepared by dis-

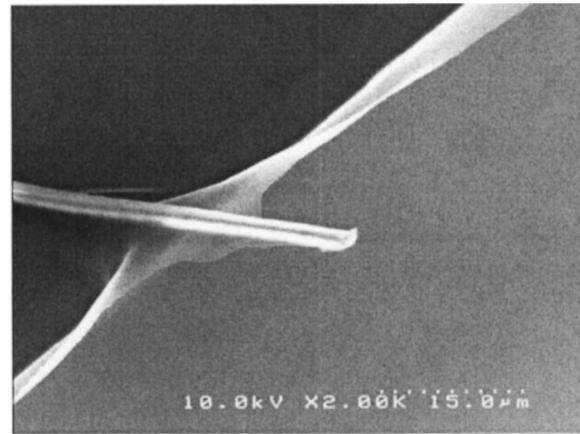


FIG. 2. Scanning electron microscope image of a waveguide, and the surrounding residue, overhanging a cleaved silicon substrate.

solving a polycarbonate, poly[bisphenol A carbonate-co-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate] (Aldrich) in dibromomethane, CH₂Br₂, in varying concentrations from 7.2 to 0.45 wt %. The polycarbonate is of practical interest as it is the same polymer host material used in the state-of-the-art electro-optic guest–host systems.⁶ Drop-lets of volume 50 μL are placed on the bare silicon and, as the mold is depressed, the force exerted on the mold is monitored with a force gauge. After 20 min, the solvent has escaped through the PDMS mold, curing the waveguide structures. The mold is released and removed from the substrate, revealing the waveguide structures [Fig. 1(f)]. The molded replica device is baked at 100 °C for 2 h to remove any remaining solvent.

III. NUMERICAL SIMULATIONS

As seen in Fig. 2, the replica molding process of polycarbonate ridge waveguides results in an undesired background residue film. It is crucial to know to what extent this residue impairs the performance of integrated optical devices. Several test cases can be investigated using simulation tools. Here we study the effects of the background residue on three fundamental properties important for integrated optical waveguide devices: the modal properties of individual waveguides, the output coupling ratio in directional couplers, and the radiation loss due to the curvature of waveguide bends.

Of basic interest for any guided wave device are the modal properties of an individual waveguide, described chiefly by the mode effective indices $n_{\text{eff}} = \beta/n$. Since the mode effective indices are governed in part by the cross-sectional shape of the waveguide, it is expected that the presence of the residue will alter the modal properties of the waveguide. For effective indices below the bulk refractive index of the cladding material, the mode is cut off and will not be guided. Further, modes that are near cutoff are more weakly guided and typically exhibit more propagation loss. The effective indices of the several lowest-order modes are calculated using a semivectorial finite-difference method

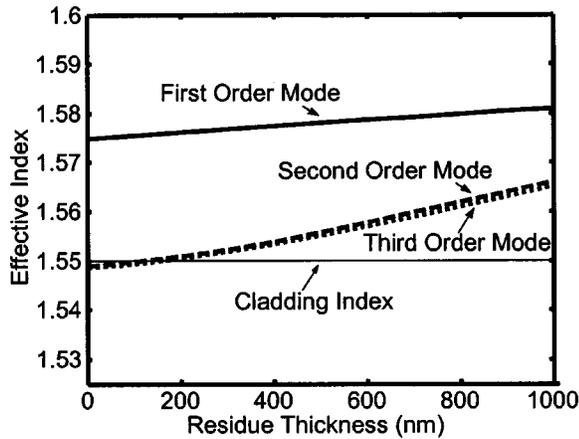


FIG. 3. Effective indices of the first, second, and third order mode as a function of residue thickness.

mode-solving algorithm¹⁷ for residue thicknesses varying from 0 to 1 μm . The waveguide is taken to have a 2.5 μm square cross section, independent of the residue, with core index 1.6. The cladding index of 1.55 is chosen to ensure single-mode operation for transverse-electric polarized light at 1550 nm, with no residue present. Figure 3 shows the results of the calculations. The first-order mode is guided for all values of the residue thickness, and the effective index increases as the residue increases in thickness. The second- and third-order mode effective indices become larger than the cladding index when the residue thickness is approximately 200 nm, however, at this residue thickness these modes are presumed to be weakly guided and exhibit high propagation loss. For thicker residues, the effective indices of these higher-order modes become significantly greater than the cladding index and are thus more strongly guided. These modes would degrade device performance through mode mixing. From these results, we find that for preventing multimode behavior, restricting the residue thickness is important. If the residue cannot be restricted, it is important to know the thickness so the other waveguide dimensions can be reduced appropriately to ensure single mode guiding. For the parameters used in this example, limiting the residue thickness to several hundred nm is essential, but for different waveguide cross sections this value could be more or less, depending on how close the higher-order modes are to cutoff.

Directional couplers are passive devices that divide input light between two output waveguides due to the proximity of the waveguides. As such, directional couplers form fundamental elements in Mach-Zehnder modulators, optical switches, and lattice filters.¹⁸ The proportion of light coupled from one waveguide to another is determined by the field amplitude overlap integral. Because this overlap integral is determined by the individual waveguide field profiles, the results of the previous section suggest that the output coupling ratio should be strongly affected by the presence of a residue. To study the effects of the residue on the performance of optical couplers, a finite-Fourier-transform beam propagation method algorithm¹⁹ is used to calculate the cou-

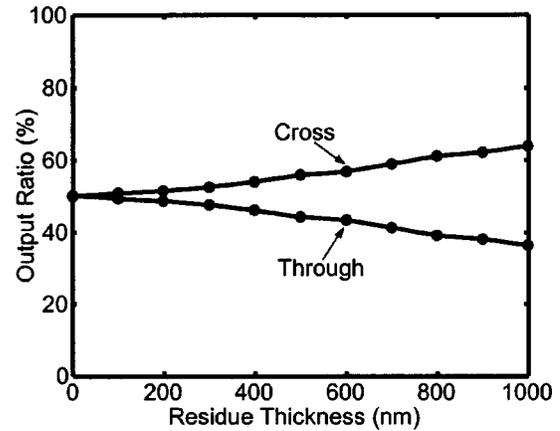


FIG. 4. Output ratio of a directional coupler as a function of residue thickness.

pling output ratio for varying residue thickness. Two waveguides, each of the same cross section and refractive indices as in the previous section, are separated by 1.4 μm for a coupling length of 147 μm . The separation and coupling length are chosen as such so light input into one waveguide results in an output coupling ratio of 50% (3 dB coupling) with no residue. The results of the calculation, shown in Fig. 4, indicate that indeed the output coupling ratio increases with increasing residue thickness. For small residue thicknesses the deviation from the desired 3 dB coupling is small, but for residue thicknesses greater than a few hundred nm, the deviation becomes significant. This is due to the fact that as the residue thickens, more of the individual mode field amplitude occupies the area shared by both individual modes and therefore the overlap integral is increased.

Waveguide bends are integral in nearly all integrated optical circuits. More specifically, a waveguide that bends back upon itself forms a ring resonator that exhibits resonances periodic in wavelength, each occurring when light acquires a phase equal to an integer multiple of 2π radians. Such structures are used for channel-dropping filters,²⁰ intensity modulators,²¹ and dispersion compensators.¹⁸ For a given bend radius, bend loss is predominantly determined by the degree of confinement. As the residue thickness increases more of the field occupies the residue, which is not laterally restricted by the refractive index, so it is expected that the bend loss significantly increases as a function of the residue thickness. To test this supposition, an azimuthal beam propagation algorithm²² is used to calculate the bend loss by monitoring the remaining field amplitude in the waveguide after each revolution of the optical field. As in the previous two calculations, we take the waveguide cross section to be 2.5 μm square with core and cladding indexes of 1.6 and 1.55. The bend radius is 400 μm , chosen because it gives essentially no bend loss for the ring without residue. The results of the calculation, Fig. 5, show that bend loss is a dramatic function of the residue thickness. For residues up to 400 nm, the bend loss is less than 1 dB/revolution, however, the bend loss quickly increases to unacceptable levels for residues thicker than 400 nm.

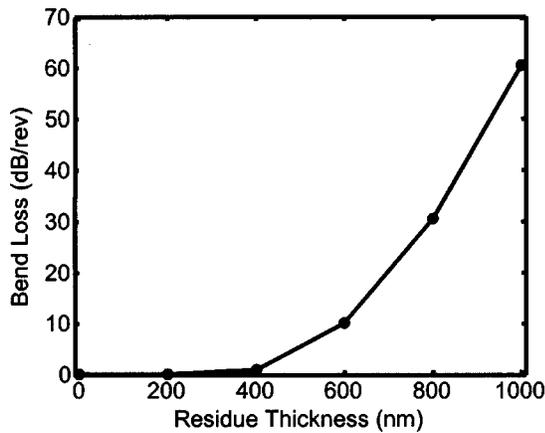


FIG. 5. Bend loss as a function of residue thickness.

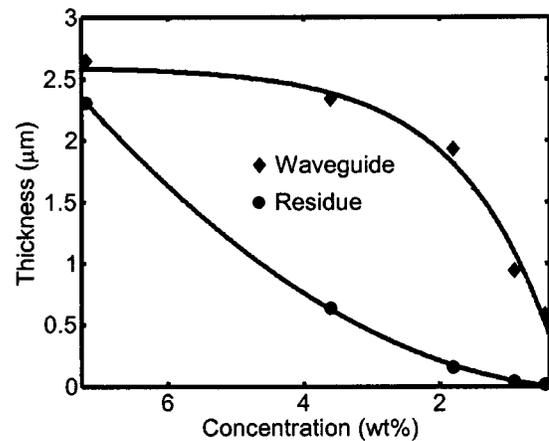


FIG. 6. Waveguide and residue thickness for various solution concentrations.

IV. REDUCTION OF THE RESIDUE

The reduction of the residue is of paramount importance for replica molding to be a useful technique for polymer waveguide fabrication. The previous simulations have shown that while small residue thicknesses are tolerable in many cases, as the residue becomes thicker the waveguides may exhibit multimode behavior, directional couplers will not divide light as intended, and waveguide bends will exhibit unacceptably high loss. In defining what variables are at hand for reducing the residue, there exist several plausible possibilities. Two apparent means of reducing the residue thickness are changing the concentration of the polymer solution or the force with which the mold is depressed. Although chemical or plasma etching is a possible treatment for reducing the residue, this adds a costly step to the otherwise simple fabrication procedure and introduces spurious effects such as changing the surface features, such as smoothness, and reducing the waveguide thickness. Another possibility that must be immediately disregarded is the change in the shape or size of the structures. The waveguide structures cannot be modified because the dimensions are determined by the modal waveguide requirements, for instance, as required for the optical device. However, previous results suggest that typical polymer optical waveguide dimensions are in the correct size and shape regimes to avoid mold deformations: the waveguides are thin enough so that there is no sagging of the mold, but wide enough and separated enough to avoid lateral deformations of the mold.²³

The solution concentration is an obvious candidate for reducing the residue, as the residue thickness will be dependent on the solution viscosity and density. Previously, dilution of a resist solution was used to reduce the residue in soft molding of etch resist, allowing a single-step etch to pattern a silica substrate.²⁴ To determine the functional dependence of the solution concentration, we mold amorphous polycarbonate waveguide structures using several concentrations of the polycarbonate solution. A stock solution of 7.2 wt% polycarbonate in dibromomethane is diluted in factors of two resulting in concentrations of 7.2, 3.6, 1.8, 0.9, and 0.45 wt%. Each solution is used to mold the waveguide structures

with a constant force of 50 N applied to the mold in each case. Upon solvent evaporation and removal of the mold, it is visually clear that the background films are greatly reduced by reducing the solution concentrations. A stylus profiler is used to precisely measure the thickness of both the background residue and the waveguide for each of the test samples. The thicknesses at several locations, the same for each sample, were measured and averaged. The measurement results are shown in Fig. 6. The residue thickness is strongly reduced by decreasing the concentration of the solution, suggesting that carefully selecting the appropriate solution concentration is a good means of reducing, or controlling, the residue thickness. The cost of reducing the residue by thinning the solution, however, is the reduction in the thickness of the waveguides for very low concentrations. This is because for low concentrations there is not enough solid in the volume of solution that fills the waveguide mold and so the condensed solid volume is much less than the intended thickness.

The mechanism that results in the residue appears to be trapping of solution between the mold and the substrate, forming pockets within which the solid residue forms. It is reasonable to assume that the force with which the mold is depressed may be a useful parameter for the reduction of the background residue because higher force would drive out more of the trapped solution. We mold several waveguide structures, using a similar procedure as above, but at a constant concentration (1.8 wt%), for various forces applied to the mold (2–100 N). The corresponding range of pressures on the mold is 3×10^4 (0.3) to 1.46×10^5 Pa (14.6 N/cm²). When the samples are cured, the mold is removed and the film and waveguide thicknesses are measured with a stylus profiler. The results are shown in Fig. 7. The thickness of both the residue and the waveguide are changed very little over a wide range of applied forces, demonstrating that the force applied to the mold is not a useful means for reducing the residue. Since the residue is very weakly affected by the force on the mold, we must consider two other observed effects that could potentially degrade device performance. First, for low forces, the mold did not make conformal

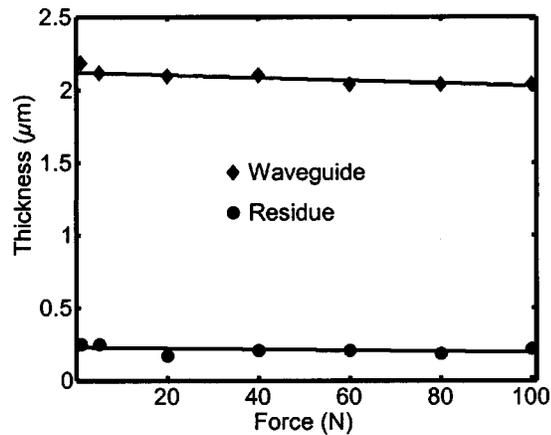


FIG. 7. Waveguide and residue thickness for various forces applied to the mold.

contact²⁵ with the substrate and a very thick residue was often observed at an edge or corner of the molded area. Second, for very high forces the mold began to deform around the edges, distorting the device features at the extremities of the mold.

As proposed, the mechanism for the formation of the residue is due to the soft and flexible nature of the PDMS mold. As the mold is depressed, the solution on the substrate is forced into the waveguide structures and the excess escapes to the edges of the mold. What solution does not escape, however, forms pockets surrounding the waveguides by flexing the mold in these regions upwards, as shown in Figs. 8(a) and 8(b). The regions of greatest rigidity to vertical forces are the sidewalls of the waveguide structures, and although they might deform laterally slightly, they do not buckle, and so are still in close contact to the substrate. Therefore in the regions immediately surrounding the waveguides, the residue is thinnest and is thickest between two far-apart waveguides. In Fig. 8(c), we show a top-view microscope image of a molded waveguide. The previous phenomenon is observable in this image: the dark colored waveguides are immediately surrounded by light color, corresponding to a very thin residue. Further from the waveguide, the residue gets thicker, shown as a darker color. The ramifications of this effect in soft-mold replica molding are significant for optical applications. The simulations presented above are worst-case, upper-bound scenarios and the actual waveguide performance is better than what the simulations predict. This result does not invalidate the importance of reducing the background residue, however.

V. CONCLUSION

In conclusion, soft lithography replication is a good technique for inexpensive, fast, mass fabrication of polymer integrated optical devices. The resolution requirements have been previously demonstrated. The major remaining fabrication difficulty preventing widespread polymer device replication is the unavoidable residue remaining after the molding process. For rational polymer waveguide cross-sectional pa-

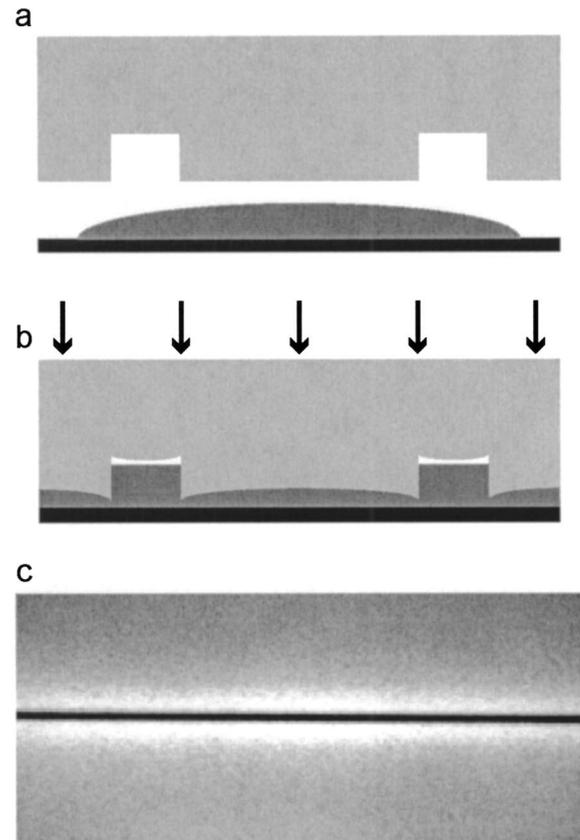


FIG. 8. Formation of background residue. In (a) the PDMS mold and polymer solution before molding. In (b) the mold is pressed atop the solution/substrate, forming the waveguide structures, but leaving a polymer residue layer surrounding the waveguides. In (c), optical microscope image showing a waveguide (black) surrounded by thin residue (white) that gets thicker farther from the waveguide (gray). The measured thicknesses correspond to the gray areas, the areas of thickest residue.

rameters, we calculate that a small residue, up to several hundred nm, is tolerable. Beyond several hundred nm of residue, waveguides become multimode, directional couplers do not exhibit the intended coupling ratios, and waveguide bends exhibit exorbitant losses. To correct the problem of the residue, the use of dilute polymer solutions greatly reduces the residue. Applying more force to the mold during the formation of the waveguides does not affect the thickness of the residue. The force does affect the conformal contact of the mold to the substrate. Finally, the molded devices yield structures with the residue being thinnest immediately surrounding the waveguides because for the aspect ratios of waveguides, there is little lateral deformation of the mold and no buckling of the waveguide walls. The thinness of the residue surrounding the waveguides will tend to reduce the deleterious effects predicted by the simulations.

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