# Microfabrication and Characterization of Teflon AF-Coated Liquid Core Waveguide Channels in Silicon

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*Abstract*—The fabrication and testing of Teflon AF-coated channels on silicon and bonding of the same to a similarly coated glass wafer are described. With water or aqueous solutions in such channels, the channels exhibit much better light conduction ability than similar uncoated channels. Although the loss is greater than extruded Teflon AF tubes, light throughput is far superior to channels described in the literature consisting of [110] planes in silicon with 45° sidewalls. Absorbance noise levels under actual flow conditions using an LED source, an inexpensive photodiode and a simple operational amplifier circuitry was $1 \times 10^{-4}$ absorbance units over a 10-mm path length (channel 0.17-mm deep $\times$ 0.49-mm wide), comparable to many commercially available macroscale flow-through absorbance detectors. Adherence to Beer's law was tested over a 50-fold concentration range of an injected dye, with the linear $r^2$ relating the concentration to the observed absorbance being 0.9993. Fluorescence detection was tested with fluorescein as the test solute, a high brightness blue LED as the excitation source and an inexpensive miniature PMT. The concentration detection limit was $3 \times 10^{-9}$ M and the corresponding mass detection limit was estimated to be $5 \times 10^{-16}$ mol.

## I. INTRODUCTION

SENSORS that rely on measurements of the liquid phase are important in chemical and biological monitoring. The most widely applied class of analytical techniques in the solution phase involves optical absorbance and fluorescence measurements. Since the range of wavelengths accessible by solid-state sources is continuously expanding, particularly into the ultraviolet, [1] and the fact that such sources (as well as solid state detectors) can be readily integrated with microfluidic devices, the optical measurements of liquid phase specimens will continue to show great promise for developing miniaturized sensors. However, optical measurements, especially absorbance, must overcome the sensitivity limitations associated with the short optical path lengths. To achieve long path lengths for chip-scale systems, so-called Z-path cells can be fabricated. However, light loss is especially severe in small cross section channels due to

absorption of light by the channel walls and their less than ideal reflectivity. Verpoorte *et al.* [2] etched silicon to produce microchannels with smooth [111] planar surfaces to improve wall reflectivity. More recently, Tiggelaar *et al.* [3] etched channels in silicon having surfaces (45° sidewalls) and coated them with 40-nm thick Pt layers. They obtained photocurrents of 20 nA for path lengths of 5–7 mm and cross-sectional areas of 0.14 mm$^2$.

A different solution to the same problem of light loss to the wall has also been recently available. This is to make the optical measurement cell behave as an optical fiber, i.e., such that there is total internal reflection at the walls and the attenuation of light due to passage through the cell is primarily due to absorption by the analyte. Such a situation is achieved if the light-carrying liquid core is bounded by optically transparent walls that are made of a material with a refractive index (RI) *less* than that of the liquid core. Recently, a series of amorphous copolymersn [4]–[6] of polytetrafluoroethylene (PTFE) with 2,2-bis-(trifluoromethyl)-4,5-difluoro-1,3-dioxole has become commercially available. These polymers, generically called Teflon AF, are optically transparent and have a RI of 1.29–1.31, slightly lower than that of water (1.33). Either Teflon AF tubes, or Teflon AF-coated glass/fused silica capillaries, behave as liquid core wave guides (LCW) when filled with water or aqueous solutions when the liquid RI exceeds that of the polymer. The fact that Teflon AF LCW-based systems permit uniquely powerful fluorescence [7]–[12], chemiluminescence [13], [14], Raman [15]–[20] and absorption detection [24]–[33] capabilities is beginning to be widely exploited albeit not yet on the chip scale. Unique applications of LCWs based on plastic or glass capillaries coated with Teflon AF or tubes made of Teflon [34], [35] have also been described.

LCWs fabricated at the chip-scale have numerous potential applications ranging from high-throughput drug screening to clinical diagnostics and gene analysis. [36] We report here on the fabrication and testing of chip-scale Teflon AF-coated LCWs in microchannels etched in silicon substrates.

## II. EXPERIMENTAL DETAILS

### A. Reagents

Chemicals used (KOH, acetone, ethanol, HF) were electronic grade from Fisher Scientific (Fairlawn, NJ) except as stated. Perfluorooctyltrimethoxysilane (0.4% solution in a high boiling fluorocarbon solvent, FluoroSy FSM 660) was obtained from Cytonix, Beltsville, MD. Teflon AF, 2400,

1600, 1601S were obtained from Dupont (Wilmington, DE). Perfluoro(n-butyltetrahydrofuran) (FC-75) was obtained from 3M Corp (Minneapolis, MN).

## B. Etching Channels in Silicon

The 2-in silicon (thickness ~660–690 $\mu$m) wafers (Silicon Inc., Boise, ID) and 2-in Pyrex glass (RI 1.473) wafers (Precision Glass & Optics, Santa Ana, CA) were used as substrates. The channels are etched only on the silicon, the glass serves as a cover plate. The silicon wafers were wet-oxidized for ~5 h, forming a ~0.9–1.0 $\mu$m oxide layer on wafer front and back. The oxide layer serves as a hard mask during the subsequent wet etching of Si. The front-surface resist was patterned with both straight and curved channels (radius of curvature $r_c$ of 6.1 and 1.9 cm, respectively) with a fixed channel width (at the top, the sidewalls are $\langle 111 \rangle$ planes angled at 5.47°) of 500 $\mu$m. The backside of the wafer was also coated with photoresist to protect the oxide layer. A positive photoresist (S 1813, Shipley, Marlborough, MA) was used in this work. This prevented undesirable etching from the wafer backside during wet etching. After the photoresist was patterned and developed using standard photolithography processing, the exposed oxide was etched by dipping the wafer in a buffered oxide etch solution, [37] diluted 1:1 with deionized water. Exposed silicon was etched at 80 °C with 25% KOH (water bath) to form channels in silicon. Etching for ~5.5 h under these conditions produced a channel depth of ~180 $\mu$m. At this point, the oxide hard mask was removed from both the front and back of the Si wafer with 20% HF. Finally, the wafer was thoroughly cleaned with a standard acetone, alcohol, and DI water rinse.

## C. Adhesion Promoter Coating

Teflon AF perfluorodioxole copolymers are nonpolar, contain no reactive chemical functionality, and are highly resistant to chemical attack. Thus, adhesion to substrates depends primarily on physical rather than chemical interactions [6]. In particular, Teflon AF exhibits practically no adhesion to untreated glass or Si surfaces. Two approaches were investigated to improve the adhesion of Teflon AF to Si and glass. We have used thin fluorocarbon films [38], [39] formed by plasma-enhanced-chemical vapor deposition (PECVD) using inductively-coupled high density plasma (HDP) methods [40]–[42]. Chemically active fluorine bonds in the plasma-generated fluorocarbon films promote the improved adhesion of Teflon AF to glass or silicon surfaces.

A simpler method relies on perfluorooctyltrimethoxysilane (0.4% solution) spin-coated onto silicon or glass. [43] The coated wafers were immediately baked at 90 °C for 10 min in an oven. Teflon AF was then spin-coated and exhibited good adhesion.

## D. Coating of Teflon AF

Three types of Teflon AF, namely 2400, 1600, 1601S (Dupont), were used for the fabrication of the LCWs. Relevant properties of these materials are listed in Table I. Dress *et al.* calculated that a ~5$\mu$ thick film is necessary to confine the light to the liquid core [44]. Because of the low solids content

TABLE I
RELEVANT PHYSICAL PROPERTIES OF TEFLON AF COATINGS INVESTIGATED

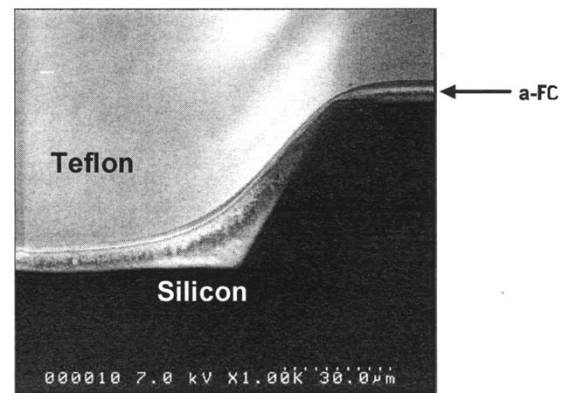| Teflon AF type (Solution) | 2400 | 1600 | 1601S |
|---|---|---|---|
| Viscosity (Pa-Sec) | 540 | 2657 | 5500 |
| Glass transition Temperature $T_g$ (°C) | 240 ± 10 | 160 ± 5 | 160 |
| Refractive Index | 1.29 | 1.31 | 1.31 |
| Concentration | 2 wt% solid | 6 wt% solid | 18 wt% solid |



Fig. 1. Scanning electron micrograph of the Teflon AF-coated channel on a silicon wafer, shown in cross section. The adhesion promoting fluorocarbon layer is not visible at this scale.

and low viscosity of Teflon AF 2400, multiple coatings were needed to obtain a 1$\mu$ thick film. For Teflon AF 1600, a single coating produced a film thickness of ~ 1.2 $\mu$m. Multiple coatings were needed with either Teflon AF 2400 or 1600 to obtain films with the necessary >3 $\mu$m thickness. The wafer was baked at 112 °C for 5 min after each spin coating, for partial removal of the solvent. This procedure produced films that were not uniform in thickness. In contrast, the high viscosity and high polymer concentration of Teflon AF 1601S resulted in 15-20$\mu$ thick and uniform films with a single coating. The RI of these films, measured using a prism coupler operated at 632.8 nm, was 1.30. In order to reduce the thickness of the coated films, the solution was diluted using FC-75. The spin speed and Teflon AF 1601 to FC-75 ratio were varied to obtain films with thickness in the 1–20 $\mu$m range. For the results presented here, we used a 2:1 Teflon AF 1601S:FC-75 ratio. At a spin speed of 4500 rpm, a single coating produced a film thickness of 4.4 $\mu$m. All the wafers were subjected to a baking cycle immediately after the coating step to remove the solvent as follows. a) Leave the coated substrate for 15–20 min at ambient temperature; b) bake at 112 °C for 15 min; c) bake at 165 °C for 15 min; d) bake at 330 °C for 30 min. The baking procedure is essential for the complete removal of the solvent. Interestingly, the RI of the films remained unchanged even though the films were processed at temperatures above the glass transition temperature ($T_g = 160$ °C) of the films. The baking of Teflon AF above its $T_g$ softens the polymer and produces a smooth surface. A scanning electron micrograph of the cross section of the Si-channel coated with Teflon AF is shown in Fig. 1. A coating that conforms to the channels is evident.
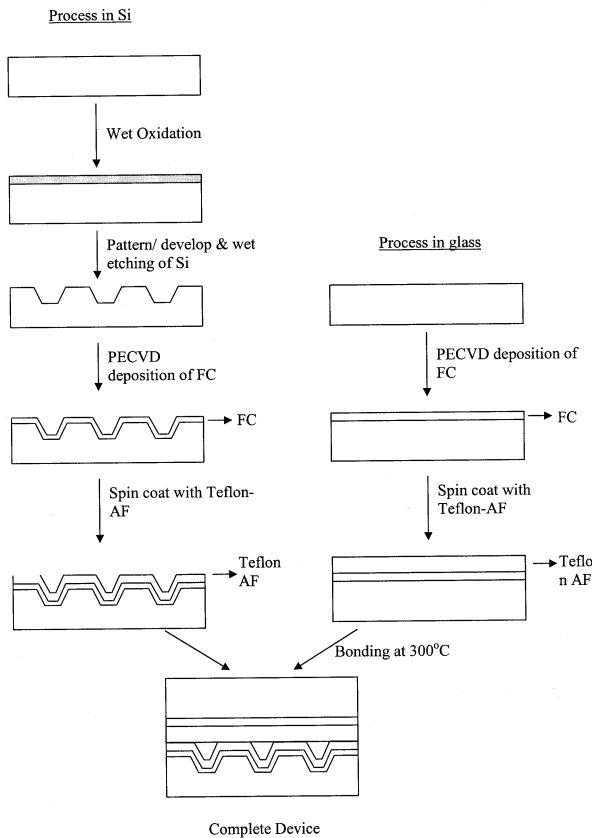
Process in Si

Wet Oxidation

Pattern/ develop & wet etching of Si

Process in glass

PECVD deposition of FC

PECVD deposition of FC

→ FC

→ FC

Spin coat with Teflon-AF

Spin coat with Teflon-AF

→ Teflon AF

→ Teflo n AF

Bonding at 300°C

Complete Device

Fig. 2. Process flow schematic. Fabrication of a bonded liquid core wave guide (LCW) device fabricated on Si.

*E. Cover Bonding for Sealed LCW and Control Devices*

The Si wafer containing 180-$\mu$m deep and 500-$\mu$m wide channels and a Pyrex glass wafer, without channels, similarly coated with Teflon AF, as described in the previous section, were used to fabricate a sealed channel. Access holes to the channels had been made on the glass wafer with a 0.75-mm diamond-tipped drill bit, using a programmable drill press, before coating the wafer with Teflon. No modification of the coating procedure from that used for the silicon wafer was found necessary for coating the drilled glass wafer. The Teflon AF-coated Si and glass wafers were aligned face-to-face and clamped together. The whole assembly was put into a furnace at 300 °C for 30 min and cooled to room temperature before removing the wafers from the clamping fixture. The sealed channels were leak-checked with water. The complete process flow diagram is depicted in Fig. 2.

A control device was made using uncoated (no Teflon AF) Si channels capped with a glass wafer. The control wafers were bonded to each after coating with 0.4-$\mu$m thick poly-methyl-silsesquioxane spin-on-glass (SOG) (Filmtronics Inc., PA), with an R.I. very close to that of glass. The SOG was spin-coated at 3500 rpm for 30 s. This SOG was chosen because it flows at relatively low temperature (150 °C–210 °C). Bonding was carried out for 3 h at 300 °C.

*F. Light Transmission Measurement*

A high brightness 660-nm light emitting diode (H-2000L, 5 mm, rated to have a luminous output of 2000 mcd, when driven

at 20 mA, input power 36 mW; Stanley Electric, Tokyo, Japan) was modified by removing most of the plastic encapsulant. A 0.5-mm diameter hole was drilled under a microscope from the top of the LED to near the emitter surface, with the LED powered and where the highest emitted light intensity was observed, taking care to not damage the emitter chip or the bonding wire. A short (5 cm) bundle of 13 70-$\mu$m diameter glass optical fibers was put together, inserted into a Teflon (0.25 mm i.d.; 0.5 mm o.d.) tube as a sleeve and held in place with silicone rubber adhesive.The fibers and the sleeve tubing were affixed into the hole with optical-grade, UV-cure adhesive (Type 81, Norland Products, Cranbury, NJ). The LED assembly was then covered with opaque epoxy (2-part epoxy, 1-part activated carbon) to eliminate ambient light. The free end of the fiber bundle was inserted into the channel under test and sealed in place with silicone rubber. This adhesive is removable and permits reuse of the fiber bundle. A similar fiber bundle was used at the other end of the channel, with the distal end epoxied to a small (4 × 5 mm) photodiode (BPW34, Siemens), similarly sealed with black epoxy. The fiber bundle is fragile and movement of the fibers during measurement can cause noise/changes in signal. A small piece of acrylic sheet was used as a support and the fiber bundle was affixed thereon. The photocurrent was measured with a picoammeter (Keithley Instruments, model 480).

The channel under test in the control wafer was filled with deionized water ensuring that there were no air bubbles and the photocurrent measured with the LED driven at 20 mA. The fiber bundle was then moved over to the corresponding channel in the LCW coated wafer. The transmittance was repeatedly measured in the corresponding channels in the respective wafers.

We also conducted direct transmission loss measurement as a function of channel length. Direct transmission loss measurement, as a function of length through the channels, is difficult because repeated movement of fibers can scratch channel surfaces and impair performance. The tube/channels were filled with a dilute solution of fluorescein and illuminated transversely at a measured distance from the exit using a near UV (385 nm) LED (UV-LED E1L5M, Roithner Lasertechnik) driven at 2.5 mA and focused to a spot approximately 100 $\mu$m in diameter. Light emerging from one end of the tube/channels was imaged on a miniature CCD spectrometer (USB 2000, Ocean Optics Inc., Dunedin, FL). The fluorescence emission intensity at 540 nm is measured varying the distance of the LED illumination point from the tube/channel (observation) end. Measurements made on both the Teflon AF-coated and uncoated control micro-channels were compared with those made on a commercial Teflon AF tube with i.d. of 0.25 mm.

*G. Measurements in a Flow Injection Analysis (FIA) Manifold*

The schematic of the FIA manifold is shown in Fig. 3. The FIA experiment used the curved LCW channel with a radius of curvature of 6.1 cm, rather than a straight channel, to reject false signals arising from line of sight transmission. The fiber-to-fiber distance, including the channel curvature, was 10.4 mm. An alkaline solution of bromthymol blue (BTB, molar absorptivity at 660 nm 11 000 M$^{-1}$cm$^{-1}$, 660 nm is not the wavelength of maximum absorption for BTB), 70 $\mu$M in concentration, was used as the test analyte. A solution of
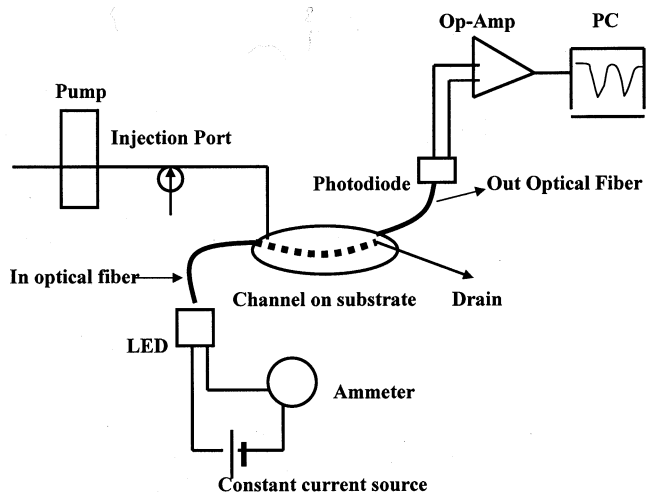
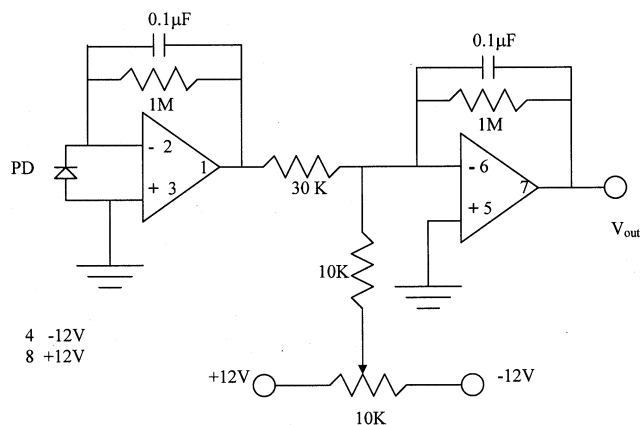Fig. 3. Arrangement for flow injection and absorbance detection, schematically shown.



Fig. 4. Absorbance detector signal processing circuit.

1 mM NaOH was used as the carrier and delivered at a constant flow rate of 47 $\mu$L/min with a peristaltic pump (Dynamax RP-1, Rainin Inc., Emeryville, CA) to the channel inlet. The analyte solution was injected using a 6-port chromatographic valve (VICI Instruments, Houston, TX). Although the actual injection loop in this valve was 20 $\mu$L, time based injection was used to inject a smaller sample volume, estimated to be $<8$ $\mu$L. Rather than using a commercial current amplifier, we opted to use what could be easily and inexpensively incorporated on a wafer-scale device. An inexpensive dual JFET operational amplifier (TL082, Texas Instruments) was used to provide both gain and offset to the photodiode output. The electronic circuitry is schematically shown in Fig. 4. The amplifier output was acquired and displayed on a notebook PC using a 12-bitA/D card (PC-CARD-DAS16/12AO, Measurement Computing Corporation, Middleboro, MA) with a data acquisition rate of 1 Hz. Conformity to Beer's law was measured by injecting different concentrations of BTB into the test system and converting the transmittance signal to absorbance (the baseline signal was taken as $I_0$).

Applicability to fluorescence detection was ascertained by coupling a high current, high intensity blue LED (Luxeon Emitter LXHL-BR01, center wavelength: 455 nm, Lumileds

TABLE II
LIGHT THROUGHPUT (PHOTOCURRENT) IN THE LCW VERSUS THE CONTROL WAFER CHANNELS

|  | LCW ( I, nA) | Control (I, nA) | Ratio |
|---|---|---|---|
| (a) straight channel (F-F[b] 23 mm) | 211 (8.2%)[a] | 13.0 (11%)[a] | 16 |
| (b) curved channel 1 ($r_c$ 6.1 cm, F-F 19 mm) | 111 (11%)[a] | 0.61 (48%)[a] | 182 |
| (c) curved channel 2 ($r_c$ 1.9 cm, F-F 19 mm) | 0.93 (8.6%)[a] | 0.11 (9.1%)[a] | 8.5 |
| (d) curved channel 2 ($r_c$ 1.9 cm, F-F 10 mm) | 8.8 (6.8%)[a] | 1.36 (19%)[a] | 6.5 |

[a] the parenthetical number indicates the RSD of 3 measurements with fresh fiber placement each time.

[b] Straight line fiber to fiber distance

LLC, San Jose, CA) driven at 250 mA to a 3-mm sapphire ball lens (manufacturer's specification on this LED: typical luminous flux 4 lm when driven at 350 mA with a junction temperature of 25 °C). The LED was placed in an opaque holder such that light was emitted only through the lens. The LED, with its holder, was placed on a small piece of blue plastic filter (# 863, Edmund Scientific, Barrington, NJ). This assembly was placed on the wafer at the channel location with an optical aperture created by black electrical tape, located ~mm from the light collection fiber optic bundle inserted into the channel. The distal end of the bundle was connected to a miniature photomultiplier tube (PMT, H5784, Hamamatsu Co.) covered with a filter stack. A combination of a yellow plastic filter (#809, Edmund) and a long-pass glass filter (KV500, Schott Glass Technologies. 50% cut off at 500 nm) was used to limit the wavelength range passed to the PMT. Flow injection was carried out by injecting ~20 $\mu$L of fluorescein, at specified concentrations, with 1 mM NaOH carrier fluid flowing at 70 $\mu$L/min.

## III. RESULTS AND DISCUSSION

### A. Light Throughput

Compared to the 5–7 mm path lengths used by Tiggelaar *et al.* [3], we tested the light throughput under the following conditions: a) straight channels, 23 mm; b) curved channel 1 ($r_c$ = 6.1 cm), fiber-to-fiber path length 19.5 mm; c) curved channel 2 ($r_c$ = 1.9 cm), fiber-to-fiber path length 19.9 mm; and d) curved channel 2 ($r_c$ = 1.9 cm), fiber-to-fiber path length 10.4 mm. The light throughput cross section is 0.067 mm$^2$ for the control wafer and 0.062 mm$^2$ for the LCW wafer. The results, that include the relative standard deviation (RSD) of triplicate measurements in each case, are shown in Table II. The LCW effect is apparent in both the straight and the curved channel with $r_c$ = 6.1 cm. The results for the highly curved channel with $r_c$ = 1.9 cm are significantly poorer. The commercial LCW tube demonstrated nearly constant throughput for curvatures down to $r_c$ = 3.0 cm. Below this curvature, geometric deformations occur in these tubes and tests could not be conducted. It may be noted that with a 19-mm source-detector separation, standard laboratory polyethyelene tubing showed negligible throughput regardless of curvature.

For the transverse illumination studies, we measured the fluorescein emission peak intensity (at 540 nm) versus distance between illumination point and tube/channel end for straight chan-

nels. In all cases, the data fit well an exponential decay pattern according to $I = I_0 e^{-\alpha L}$ where $I$ and $I_0$ are the transmitted and incident light intensities, L is the lateral distance between the transverse illumination source and the detector and $\alpha$ is the attenuation coefficient. Values of $\alpha$, corrected for the attenuation of the fluorescein solution (measured to be $180\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) were $0.07 \pm 0.01$, $0.25 \pm 0.01$, and $1.09 \pm 0.01$ cm$^{-1}$ for the commercial tube, the coated channel and the uncoated channel, respectively. While the coated microchannels are not as good light conduits as the extruded tubes, they are substantially superior to the uncoated channels, as found in the longitudinally launched absorption measurements, summarized in Table II (b).

There is a greater light loss in the coated micro-channels compared to an extruded Teflon AF tube because a) the channels are not of cylindrical shape which will lead to the lowest losses; in fact, the etched channels may not have exactly uniform cross-section due to variations in the etching and deposition processing over a long etching period, b) etching deep channels in silicon in this manner results in surface irregularities and all the roughness may not be entirely removed by the coating. While the postbake procedure appears to smoothen the coating, microscopic observations suggest that the surface finish is still not as good as that of extruded tubes. In any case, the light throughput in the coated case is good enough to obtain excellent analytical results as demonstrated in the following sections. It is to be also noted that for the straight channel, even though we have less than half the light throughput cross section and nearly four times the path length, the photocurrent for our straight path LCW cell is still an order of magnitude greater compared to that reported by Tiggelaar *et al.* [3], both cases using comparable LED sources.

### B. FIA Signals and Absorbance Detection Performance

Fig. 5 shows response of the system to repeated injections of the BTB solution into a flowing carrier of 1 mM NaOH. The results are shown both for the Teflon AF-coated wafer and the control wafer, offset for clarity. Approximately 1% of the signal that is observed for the LCW is observed with the control (observable only after a large magnification). This suggests that whatever light does pass through the channels probably does so by grazing angle propagation along the walls and has little relationship with the liquid core. For the LCW cell, the reproducibility of the response is good (0.9% RSD).

Without offset and at the same photodiode amplifier gain, the baseline signal in the LCW case shown in Fig. 5 would lie at $\sim$30 V. The baseline noise that we observe, part of which is clearly attributable to the A/D conversion noise (for the 12-bit A/D used in the $\pm$10 V scale, 1-bit noise is equivalent to 4.9 mV) is 7.6 mV. This translates to a transmittance noise of 0.025% T and in terms of absorbance, $1.1 \times 10^{-4}$ absorbance units, respectable for the simple circuit and the miniature cell.

The linearity and adherence to Beer's law was studied over a range of 2–100 $\mu$M BTB injected. The linearity is excellent over this $\sim$2 orders of magnitude span, with a linear $r^2$ value of 0.9993. The results are shown in Fig. 6.

Fluorescence detection was investigated to ascertain practical limits of fluorescence detection limits that can be attained by presently available inexpensive solid-state sources. One interesting aspect of transverse fluorescence detection in this
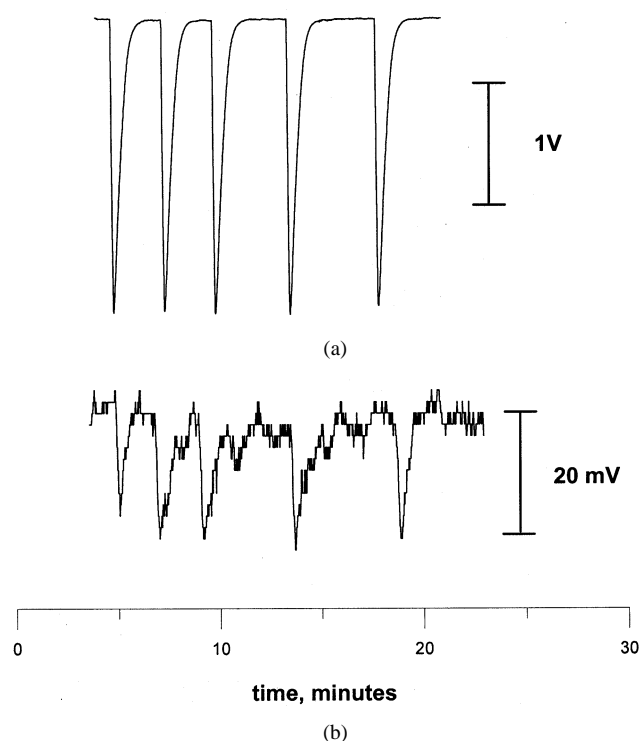


Fig. 5. Flow injection system output for repeated injections of 70 $\mu$M Bromthymol Blue ($\sim$ 8 $\mu$L) in a 1 mM NaOH carrier (47 $\mu$L/min). (a) Upper trace shows results for Teflon AF-coated channels; (b) the lower trace the same for uncoated channels, 50 $\times$ amplified and appropriately offset.
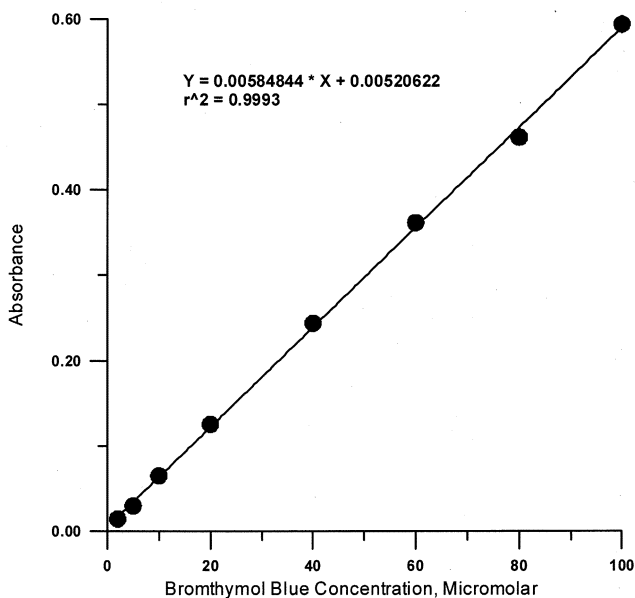


Fig. 6. Beer's law plot for different concentrations of dye injected.

manner with solid state sources is that sources emitting at different wavelengths can be aligned in an array along a channel and the excitation wavelength can be temporally scanned by serially turning on each emitter. For the present purpose of dedicated wavelength fluorescence detection, we chose fluorescein because it is an inexpensive common fluorescent tag that is used widely. The results are shown in Fig. 7 for single digit nM concentrations of fluorescein injected. We con-
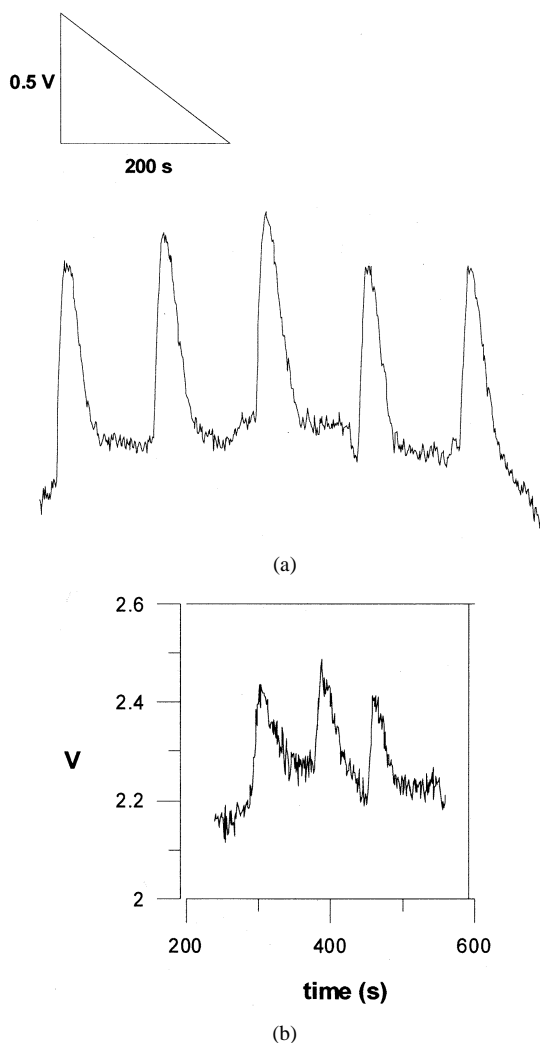
(a)

(b)

Fig. 7. Flow injection system output for repeated injections ($\sim 20\ \mu$L) of (a) 9-nM and (b) 3-nM Fluorescein sample in a 1 mM NaOH carrier (70 $\mu$L/min).

servatively estimate that the $S/N = 3$ LOD is $\sim$3 nM (inset, Fig. 7). The illuminated volume is about 0.14 $\mu$L; this results in a mass detection limit of 410 attomoles, or $\sim$250 million molecules. Given the capital cost with which this detection can be performed, we deem it to be excellent.

## IV. SUMMARY

We have developed a process for coating flat glass surfaces and etched microchannels in silicon with low R. I. Teflon AF, and successfully bonded the respective wafers to form sealed microchannels. When filled with aqueous solutions, the channels demonstrated significantly enhanced optical waveguide properties when compared to control channels identically fabricated but left uncoated. The microfabricated LCW can be used for high sensitivity measurements. Future work will refine the fabrication process to yield smoother channels for complete analysis devices.

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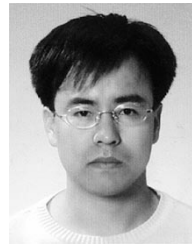
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