FACILE FABRICATION OF CALCIUM FLUORIDE IR-TRANSPARENT MICROFLUIDIC DEVICES

Brynson J. Lehmkuhl, Scott D. Noblitt, Amber T. Krummel, and Charles S. Henry
Colorado State University, USA

ABSTRACT
Infrared spectroscopy (IR) provides a wealth of chemical information. Ideally, IR could be combined with microfluidics to provide monitoring of chemical and biochemical reactions with both spatial and temporal resolution. However, few IR-compatible microfluidic devices have been produced, primarily due to the IR-absorbing characteristics of most microfluidic substrates. Here, we demonstrate IR-compatible devices composed of CaF$_2$ substrates bonded using either poly(dimethylsiloxane) (PDMS) or polymer membranes. The PDMS-bonded devices use chemical etching to create channels in the CaF$_2$, whereas the membrane-bonded microchips have laser-cut channels. The fabrication techniques employed and IR results are discussed.

KEYWORDS: Infrared, Spectroscopy, Detection, Calcium Flouride

INTRODUCTION
Infrared spectroscopy (IR) is a well established technique for probing molecular-level chemical bonding environments. With the advent of Fourier transform infrared spectroscopy (FTIR), modern spectrometers can rapidly collect data over large wavelength ranges. Some applications for IR include monitoring chemical reactions, analyzing solvation effects, and probing protein structures. Current instruments are capable of providing chemical information with either high temporal or spatial resolution; however, combinations of temporal and spatial resolution are limited. The coupling of microfluidics to FTIR spectroscopy would permit simultaneous spatial and temporal resolution with the added benefits of small sample sizes and rigorous fluid control. To date, however, there has been limited incorporation of IR with microfluidics. The main obstacle for IR transparent microfluidics is the material employed, as all common microfluidic substrates strongly absorb IR radiation and are typically present at thicknesses of $\geq$1 mm. With the exception of optically thin PDMS [1], IR microfluidic devices have been prepared in either silicon or CaF$_2$ [2]. Silicon is not visibly transparent, so CaF$_2$ is preferred for many applications. Most current IR-compatible microfluidic devices are not self-contained and require a holder to remain assembled during operation. The requirement for a holder can lower reproducibility, increase the final device footprint, and make operation more complex.

To address the need for IR-compatible microfluidic devices, particularly one that is self-contained, we have developed two simple fabrications for CaF$_2$ microchips. One approach uses nitric acid to etch microfluidic channels directly into CaF$_2$. The channel-containing substrate is then bonded to another CaF$_2$ plate using a submicron spin-coated layer of PDMS. The other method utilizes commercial membranes or adhesives for bonding. With this method, the channel is not formed in the CaF$_2$ itself, which stays flat, but instead is defined by cuts made in the membrane using a CO$_2$ laser. Both methods represent avenues for the facile fabrication of IR-transparent microfluidic devices.

THEORY
The channel depths on membrane- and adhesive-bonded devices were measured by fitting the interference fringes of an IR spectrum of an empty channel to a sinusoidal function and converting the fitted frequency ($f$) to depth ($d$) using equation 1 and the refractive index of the fluid in the channel ($n$, 1.00 for air).

$$d = \frac{f}{2n}$$
EXPERIMENTAL

Optical-grade CaF\(_2\) plates were purchased from Crystran. Polycarbonate membranes were obtained from Whatman (Nucleopore and Cyclopore membranes) and Osmonics (Poretics membranes). Adhesive sheets (467MP) were purchased from 3M. Laser cutting was executed using a Zing 30-watt CO\(_2\) laser from Epilog. Profilometry was performed with a Zygo ZeScope optical profilometer. IR data were obtained with a Bruker Hyperion 3000 IR microscope equipped with a focal plane array (FPA) detector.

Microfluidic channels in PDMS-bonded chips were etched using 1.5 M HNO\(_3\). A PDMS “etch mask” with the channel layout was first produced using traditional soft lithography. This mask was then pressed conformally to a CaF\(_2\) substrate, and the acid was flowed through the PDMS channels, etching the exposed CaF\(_2\). Etching depth depended on acid concentration, exposure time, and flow rate. The chip fabrication layout and an etched CaF\(_2\) surface profile are shown in Figure 1. The etched substrate was then bonded to the blank substrate by spin coating a toluene-PDMS (6:1) mixture on the blank CaF\(_2\), pressing the two plates together, and curing the PDMS.

The microfluidic channels in membrane/adhesive-bonded devices were laser cut, and the fabrication process for the membrane chips is illustrated in Figure 2. Cut settings varied depending on the material properties. To lay the polycarbonate membranes flat, they were placed on featureless PDMS, which also held them in place. After cutting, a few drops of 50/50 water/methanol were added to the membrane to aid in transferring it to the CaF\(_2\) substrate. After placement on a CaF\(_2\) plate, a second plate was added, sandwiching the membrane. Glass slides were placed on both sides of the chip, and the sandwich was put in a c-clamp. The clamp and chip were placed in an oven that ramped to 200 °C, held them for 30 min, then ramped back down to room temperature (ramping performed at 10 °C min\(^{-1}\)). For the adhesive-bonded chips, no clamps or oven were used. Chips were prepared using finger pressure at room temperature.

Both chip fabrication processes are reversible. The membrane- and adhesive-bonded chips are deconstructed by soaking the device in acetone, followed by pulling the substrates apart. The PDMS-bonded substrates are pulled apart after a similar soak in toluene.

RESULTS AND DISCUSSION

The PDMS-bonded devices were evaluated by imaging a two-flow system of 2,2’-bipyridine-4,4’-dicarboxylic acid (bipy-dca) and Fe(II), both dissolved in dimethylsulfoxide (DMSO). Results are shown in Figure 3. IR intensity mapping shows a strong bipy-dca signal entering from the left, an Fe(II) signal arriving from the right, and a defined interface between the two laminar flows. This example confirms the ability of these chips to obtain spatial chemical information and their ability to handle organic solvents.
Figure 3: Bright field images at a PDMS-bound channel intersection with IR intensity map overlays. Left) Bright-field image of area of interest—the bottom of the intersection. Middle and right) Bipy-dca in DMSO entered from the lower left; Fe(II) in DMSO entered from the lower right. Middle) Intensity map plotted for absorbance at 1650 cm\(^{-1}\). Right) Intensity for 2550 cm\(^{-1}\). (670-µm wide IR images.)

Because the membrane/adhesive-bonded channel depths may differ from the bonding material’s original thickness, Equation 1 was used to measure channel thicknesses (example IR data in Figure 4). Depths near 7.5, 10, 23, and 60 µm were obtainable. The 60-µm devices were produced from the adhesive with a reported 60-µm thickness. However, the 10-µm depths came from 6-µm membranes that were laser cut. We suspect membrane deformation from laser cutting causes the discrepancy. Initial testing of the 10-µm devices was performed with H\(_2\)O. Figure 4 shows a channel with overlaid intensity maps for polycarbonate and H\(_2\)O, demonstrating these devices for obtaining chemical spatial information.

Figure 4: Left) IR interference pattern for membrane-bound empty channels at several depths. Right) bright-field images (1 mm wide) of water-filled channel with intensity map overlay for IR integrations for polycarbonate (1757-1793 cm\(^{-1}\), middle) and water (1570-1711 cm\(^{-1}\), right).

CONCLUSION

We demonstrated two facile approaches for building basic IR-transparent microfluidic devices with CaF\(_2\) substrates. The PDMS-bonded fabrication approach permits features of the same complexity as attainable by traditional soft lithographic methods, and its channel depths are determined by the acidic etching procedure. The membrane/adhesive-bonded method is limited to simpler channel geometries, and channel depths are dictated by the thickness of the bonding material.

ACKNOWLEDGEMENTS

The authors thank John B. Wydallis of Colorado State University for his suggestion to try the 3M adhesives as thicker spacers and for his help operating the optical profilometer.

REFERENCES


CONTACT
* C.S. Henry; phone: +1-970-491-6865; chuck.henry@colostate.edu

2320