

gases can be directed to flow over the substrate during the ablation process to provide a desired chemical or reactive environment. In some instances, liquids can be placed on the top surface of the substrate and photo-ablation can be achieved by passing the light through the liquid. It is also possible according to the present invention to ablate through a solid on the surface of the substrate to change the functionality of the substrate beneath.

FIGS. 1a and 1b are diagrams that depict the manner in which photo-ablation is conducted under controlled atmospheres. In FIG. 1a the substrate 1 which is targeted for photo-ablation has a liquid 2 on an upper surface thereof. The laser light beam 3 passes through the liquid 2 and ablates the underlying surface of the substrate 1. The liquid can be selected to provide a chemical atmosphere, which reacts with the ablated surface of the substrate 1. FIG. 1b is similar to FIG. 1a except that instead of providing a liquid on the surface of the substrate 1, a gas 4 is directed across the surface of the substrate 1.

When using any of the above processing techniques of the present invention, the dimensions of the microfabricated features produced are limited by the spot size of the beam and the physical characteristics of the substrate, such as its absorption at the photon frequency. The present inventors have discovered that the aspect ratios attainable with the photo-ablation technique are comparable to other techniques such as X-ray micromachining, anisotropic wet etching, and silicon template imprinting. However, the amount of time required to produce a structure according to the present invention is greatly reduced due to the rapidity of the technique.

FIGS. 2a-2c are cross-sectional views of channels, which are formed by photo-ablation according to the present invention. The channel produced in FIG. 2a involved photo-ablating a substrate that was covered with water. The channel produced in FIG. 2b involved photo-ablating a substrate that was covered with methanol. The channel produced in FIG. 2c involved photo-ablating a substrate that was blanketed with a stream of nitrogen gas.

Changes in chemical functionality produced by the techniques of the present invention can be assessed using chemical mapping. Chemical mapping is a technique in which group-specific fluorescent probes are used to image functional groups on a polymer surface. During the course of the present invention, ablation effects and chemical functionality were accessed utilizing a modified fluorescein dye to image functional groups on the surface of polymer substrates (e.g., carboxylate groups on PMMA) before and after laser ablation at 248 nm. Additional chemical moieties such as amine or alcohol groups may be probed with differently modified fluorophores. The intensity of the fluorescence correlated to the density of specific functional groups on the surface before and after ablation.

FIGS. 3a, 3b, and 3c are fluorescent chemical mapping images of a PETG channel ablated under oxygen, nitrogen, and air, respectively. These figures demonstrate changes in chemical functionality produced according to the present invention. FIGS. 4a and 4b are fluorescence images of a polymer (PETG) microchannel ablated under a) methanol and b) water and then chemically mapped as described. These figures demonstrate changes in chemical functionality produced according to the present invention under a liquid atmosphere. FIGS. 3a-3c and 4a and 4b identify the change in carboxyl groups and demonstrate that the process of changing functionality according to the present invention can be verified by chemical mapping.

In addition to chemical mapping, microfluidic channels produced according to the present invention were characterized by their electroosmotic mobility, which is directly related to the surface charge that resides on the channel walls. This characteristic is important in the construction of microfluidic devices because it dictates a channel's ability to move plugs of solution. The electroosmotic mobility was measured by two methods. The first technique utilized was a current monitoring method which measures the amount of time required to displace a solution in a channel with one of another concentration. In the flow imaging method, a caged fluorophore in solution is released by a pulsed laser and imaged by fluorescence microscopy. By monitoring its migration under the influence of an electric field, the electroosmotic mobility of the channel can be ascertained.

Chemical mapping and the measurement of the electroosmotic mobility demonstrate that it is possible to vary the charge density and the distribution of functional groups by controlling the atmosphere and local chemical environment during photo-ablation. Thus, the present invention provides a process by which microfluidic channels and microvials may be constructed in various polymers under different localized chemical atmospheres to create devices that are specific towards different applications.

Using the photo-ablation technique of the present invention, various polymers were ablated under five different local atmospheres. The polymers studied included polycarbonate, polystyrene, poly (ethylene terephthalate glycol), poly (methyl methacrylate), and poly (vinyl chloride). These polymers were ablated under argon gas, nitrogen gas, oxygen gas, liquid methanol, and liquid water. As opposed to other techniques that functionalize an entire surface, the photo-ablation technique allows one to functionalize areas that are defined by the dimension of the photon area imaged on the surface. Consequently, it is possible to place different functional groups adjacently to each other during fabrication B

FIGS. 3 and 4 fluorescent images of chemically mapped channels that depict the effects of different atmospheres on surface charge. The substrates depicted in FIGS. 3 and 4 were sonicated in a mild phosphate buffer (pH=7.0) after channel ablation to remove debris, soaked in fluorescein and EDAC for 8 hours, and rinsed in phosphate buffer. The fluorescence in the FIGS. 3 and 4 is indicative of surface bound, labeled carboxylate groups. The substrate in FIG. 3b was photo-ablated under oxygen. The substrate in FIG. 3a was photo-ablated under nitrogen. The substrate in FIG. 4a was photo-ablated under air. The substrate in FIG. 4b was photo-ablated under water. The substrate in FIG. 4b was photo-ablated under methanol.

FIG. 5 is a graph that depicts electroosmotic mobility of polycarbonate under different ablation conditions. As seen from FIG. 5, microchannels ablated under methanol had the lowest electroosmotic mobility, whereas microchannels ablated under oxygen had the highest electroosmotic mobility. This indicates that the oxygen-ablated channels had a higher surface charge density that those ablated under methanol.

The present invention allows the fabrication and surface modification of polymer microdevices to be integrated into a one-step process. In addition, the localized process allows for different functional groups to be placed in close proximity on the same device. Atmospheres under which photo-ablation takes place may consist of any chemical in a solid, liquid or gas phase that may be placed in contact with the substrate surface. The chemical environment needs to exist