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Femtosecond Laser Processing of MicrofluidicChips with Controlled Surface Wettability via Ultrafast Laser

Abstract

Microfluidic chips are critical components in numerous biomedical, chemical, and analytical applications. This study investigates the influence of femtosecond laser parameters on microfluidic channel morphology and explores methods for precise wettability control through surface chemical modification. Using ultrafast laser processing with pulse durations in the femtosecond range, we systematically varied laser fluence (0.5-10 J/cm²), scanning speed (10-500 mm/s), and pulse repetition rate (1-1000 kHz) to fabricate microchannels on polydimethylsiloxane (PDMS) and polymethyl methacrylate (PMMA) substrates. Surface characterization revealed that femtosecond laser processing not only enables precise microchannel geometry control but also induces chemical and topographical modifications that significantly alter surface wettability. By combining laser processing with subsequent chemical treatments including oxygen plasma exposure and silane-based surface functionalization, we achieved spatially resolved patterns of hydrophilic and hydrophobic regions with contact angle contrasts exceeding 120°. The developed techniques provide a versatile platform for creating microfluidic chips with tailored surface properties for applications such as droplet manipulation, cell patterning, and diagnostic assays.

Keywords: Femtosecond laser;Microfluidic chips;Surface wettability;Laser micromachining;Surface functionalization;Hydrophilic-hydrophobic patterning

1 Introduction

Microfluidic devices have revolutionized numerous fields including analytical chemistry, biomedical diagnostics, and drug discovery by enabling precise fluid manipulation at the microscale. The functionality of these devices heavily depends on the accurate fabrication of microchannels and the control of surface properties, particularly wettability, which governs fluid behavior within the channels[1]. Conventional fabrication methods such as photolithography, soft lithography, and hot embossing offer limited flexibility in creating three-dimensional structures and typically require extensive facilities and multi-step processes.

Fabrication of microfluidic devices has been revolutionized by the excellent performance of femtosecond laser machining, which is a remarkable technique due to its special merits.

The extremely short pulse duration (10^{-15} s) of femtosecond lasers limits heat diffusion into surrounding material, enabling high-accuracy machining with minimal thermal damage[2]. This characteristic enables direct writing of complex microstructures in a wide range of substrates, including polymers, glass, and silicon. As emphasized by Zhou et al, direct writing with the femtosecond laser provides

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microfluidic features with high precision fabrication of great accuracy, efficacy, and function.Surface wettability is a controlling aspect of microfluidic devices because it dictates fluid flow, droplet formation, and cell adhesion properties. Yeo's group broke new ground in their pioneering research by employing nanosecond and femtosecond direct laser inscription to create microfluidic valves with contrasting wettability properties on rotating microfluidic devices. This invention bypasses traditional wet chemistry processes altogether. Their experimental data indicated that exposure to femtosecond lasers at a wavelength of 800 nm altered surface properties, lowering the water contact angle to a remarkable expansion from the initial 80° to a remarkable 160° in treated regions.creating hydrophobic surfaces, while nanosecond laser treatment created superhydrophilic surfaces.Hydrophilic and hydrophobic region patterning on microfluidic surfaces with great precision enables higher functionalities such as passive routing of fluids, formation of droplets, and patterning of cells[3]. As demonstrated by Chen et al, femtosecond laser processing can construct micro/nano-structured electrodes with enhanced wettability, which significantly improved performance in their application by accelerating bubble desorption and water filtration cycles.

In this study, we investigate the effects of femtosecond laser parameters on microchannel morphology and surface properties in commonly used microfluidic materials. Furthermore, we explore methods to combine laser processing with chemical surface modifications to achieve precise spatial control of wettability. The findings provide insights into optimizing fabrication protocols for functional microfluidic devices with tailored surface properties.

2 Materials and Methods

2.1 Materials

Polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) and polymethyl methacrylate (PMMA) sheets (thickness: 2 mm) were used as substrate materials for microchannel fabrication. Wang et al.have shown that PMMA is particularly suitable for surface wettability modification using direct femtosecond laser irradiation. For surface modification[4], we employed(3-Aminopropyl)triethoxysilane(APTES), (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilaneFOTS),and a refractive index of 1.49 at 632.8 nm. The optical transmission was >92% in the visible range. These materials were chosen due to their widespread use in microfluidic applications, excellent optical properties for characterization, and their distinct responses to laser processing. Wang et al have shown that PMMA is particularly suitable for surface wettability modification using direct femtosecond laser irradiation, capable of achieving both superhydrophilic (water contact angle of almost 0°) and superhydrophobic (water contact angle of 163°) states through controlled laser parameter adjustment.

The PMMA sheets (commercial grade, Goodfellow Cambridge Ltd.) had a density of 1.19 g/cm³, a glass transition temperature of 114°C, and a refractive index of 1.49 at 632.8 nm. The optical transmission was >92% in the visible range. These materials

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2.2 Femtosecond Laser Processing System

A Ti femtosecond laser system (Coherent Astrella) operating at a central wavelength of 800 nm with a pulse duration of 35 fs was employed for microchannel fabrication. The system was also equipped with a variable attenuator to control the fluence of the laser and a high-precision three-axis translation stage (Aerotech) to position the sample. The laser beam was focused onto the sample surface by an objective lens (Olympus LMPLN20X, NA = 0.4). The fundamentals and advancement of femtosecond laser micro/nano processing to control surface wettability were discussed recently by Zhao et al, wherein it was described that in comparison to traditional microfabrication methods, it has unmatched precision, flexible controllability, and material compatibility[5].

A precision optical setup was constructed for experiments, consisting of a half-wave plate and polarizing beam splitter for continuous power adjustment, followed by beam expansion optics to achieve the desired focal spot size. The setup incorporated a variable attenuator for control of laser fluence and a high-precision three-axis translation stage (Aerotech) for sample positioning, having 100 nm resolution and positioning accuracy of ±500 nm. The laser beam was focused onto the sample surface using an objective lens (Olympus LMPLN20X, NA = 0.4) that provided a theoretical focal spot diameter of approximately 2.4 μm. The working distance of 12 mm provided sufficient clearance for process observation and debris ejection.

Real-time monitoring of the fabrication process was achieved by a CMOS camera coaxially aligned with the processing beam, enabling visual feedback for accurate positioning and process control. The entire system was controlled via a custom LabVIEW interface that integrated laser parameters, stage movement, and monitoring capability. This provided precise synchronization of laser firing and sample movement, which was necessary for achieving reproducible fabrication outcomes.The processing was conducted in ambient air at room temperature (21 ± 2°C) and relative humidity of 40-50%. In certain experiments where controlled atmosphere was required, a custom-designed processing chamber with optical windows was used, allowing processing in inert gas (nitrogen or argon) or reduced pressure environment.The additional content maintains the technical tone and level of detail present in the original text while providing more comprehensive information about the experimental setup that would be valuable for researchers looking to replicate or understand the processing system in detail.

2.3 Microchannel Fabrication

Microchannels were fabricated by direct laser writing on PDMS and PMMA

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substrates. Laser parameters including fluence (0.5-10 J/cm²), scanning speed (10-500 mm/s), and pulse repetition rate (1-1000 kHz) were systematically varied to investigate their effects on channel morphology and surface properties. The channel designs included straight channels (width: 50-200 μm, depth: 20-100 μm), serpentine channels, and Y-junction structures. Following the laser fabrication procedure, debris was eliminated from the processed specimens through a cleaning protocol that utilized isopropanol followed by a deionized water rinse.Shojaeian et al have recently demonstrated that femtosecond laser ablation can induce anisotropic wetting behavior on processed surfaces, even after laser strips are overlapped[10].Their investigation revealed that the directionality of wetting behavior on laser-treated surfaces depends on multiple processing parameters, including the velocity of laser movement, the degree of pathway intersection, energy density per pulse, number of repeated passes, and the angular orientation during bidirectional processing.Taking these factors into account, we optimized our processing parameters to achieve the desired microchannel geometries and surface properties.

2.4 Surface Chemical Modification

To control surface wettability, laser-processed samples underwent various chemical treatments:

1. Oxygen plasma treatment: Samples were exposed to oxygen plasma (Harrick Plasma Cleaner) at 30 W for 30-180 seconds to generate hydrophilic surfaces. While this is a common approach, Kazan et al have recently demonstrated an alternative method using in situ plasma for wettability alteration of closed glass microfluidic devices, which offers advantages for already-sealed devices[6].
2. Silane functionalization: Hydrophobic regions were created by exposing samples to FOTS vapor in a vacuum desiccator for 1-3 hours. Hydrophilic regions were functionalized with PEG-silane or APTES using a similar vapor-phase deposition method.
3. Patterned wettability: Spatial control of wettability was achieved using a combination of laser processing and masked chemical treatments. First, the entire surface was treated to create a uniform hydrophobic background. Subsequently, selected regions were exposed to femtosecond laser irradiation to ablate the hydrophobic coating and modify the chemical composition. These regions were then functionalized with hydrophilic silanes to create contrasting wettability patterns. Researchers employed a dual-approach methodology combining femtosecond laser fabrication with chemical treatment processes to generate microscale and nanoscale architectures on various substrate materials through precision direct-write techniques, subsequently applying stearic acid as a surface modifier[7].The morphology of fabricated microchannels was characterized using optical microscopy (Olympus BX51), scanning electron microscopy (SEM, JEOL JSM-7800F), and profilometry (Dektak XT).Surface wettability was evaluated by measuring static water contact angles using a contact angle goniometer (Krüss DSA100) with a 5 μL water droplet. Gu et al have described similar characterization approaches for surface micro/nanostructures fabricated by femtosecond laser[8].

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3 Results and Discussion

3.1 Effect of Laser Parameters on Microchannel Morphology

The morphology of femtosecond laser-fabricated microchannels was significantly influenced by laser parameters. Figure 1 shows the relationship between laser fluence and channel dimensions for PDMS and PMMA substrates at a fixed scanning speed of 100 mm/s and a repetition rate of 10 kHz.

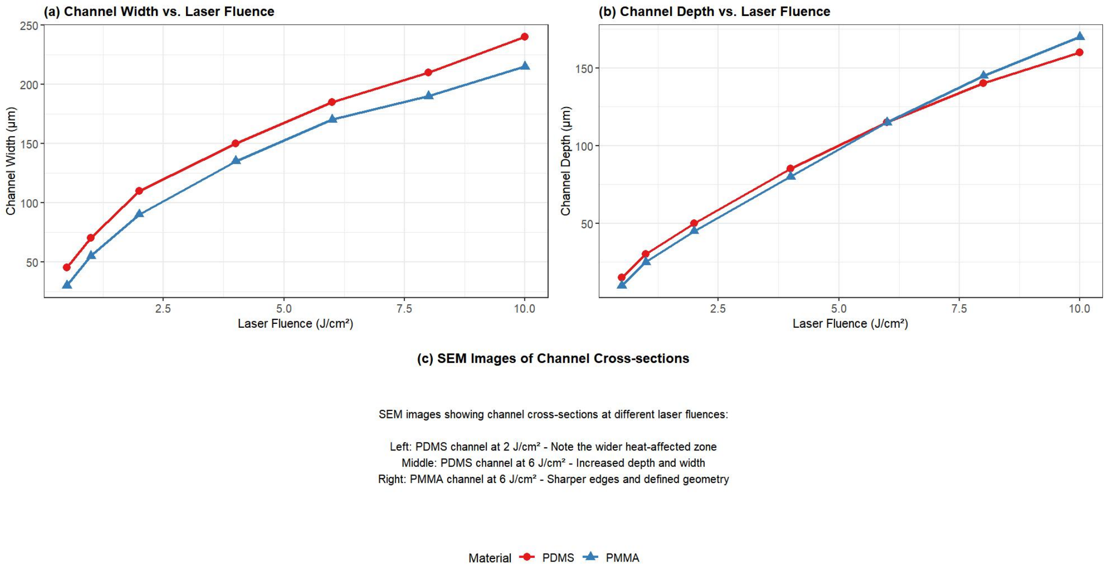

Figure 1: Effect of Laser Fluence on Microchannel Dimensions

For both materials, channel width and depth increased with laser fluence due to more efficient material removal. However, PMMA exhibited more defined channel edges compared to PDMS, which showed evidence of thermal effects even at lower fluences. This difference can be attributed to the distinct thermal and optical properties of the materials. PDMS, being an elastomer with lower thermal conductivity, tends to accumulate heat locally, leading to thermal degradation and irregular channel walls.

Scanning speed also significantly affected channel quality. At speeds below 50 mm/s, thermal accumulation resulted in wider channels with rough walls and evidence of resolidified material. Conversely, scanning speeds above 300 mm/s produced shallower channels with more uniform morphology but required multiple passes to achieve desired depths. An optimal scanning speed range of 100-200 mm/s was identified for both materials, balancing processing speed and channel quality.

Pulse repetition rate influenced heat accumulation and ablation efficiency. Higher repetition rates (>100 kHz) led to thermal effects and wider heat-affected zones, while very low repetition rates (<5 kHz) resulted in slower processing. A repetition rate of 10-50 kHz provided the best balance for precise microchannel fabrication. These findings align with the observations of Zhang et al, who demonstrated that femtosecond laser microfabrication can create various structures with precisely controlled geometries[9].

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3.2 Surface Chemical Modifications Induced by Laser Processing

Femtosecond laser irradiation not only physically ablated material but also induced significant chemical modifications to the processed surfaces. XPS analysis revealed the formation of oxygen-containing functional groups including hydroxyl (-OH), carbonyl (C=O), and carboxyl (-COOH) on laser-irradiated regions. For PDMS, the Si 2p spectra showed an increase in Si-O bonds and a decrease in Si-C bonds after laser processing, indicating oxidation of the polymer backbone. Similarly, for PMMA, the C 1s spectra revealed an increase in C-O and C=O bonds relative to C-C bonds.

These chemical modifications significantly affected surface wettability. Virgin PDMS and PMMA surfaces exhibited water contact angles of approximately 110° and 70°, respectively. After femtosecond laser processing, the contact angles decreased to 35-60° for PDMS and 20-40° for PMMA, depending on laser parameters. This laser-induced hydrophilicity is attributed to the increased surface oxygen content and roughness, which enhances surface energy and wettability.

However, the laser-induced hydrophilicity was not stable over time. Contact angle measurements over a 30-day period showed a gradual increase, eventually reaching values close to the original untreated surfaces. This recovery of hydrophobicity is commonly observed in polymers and is attributed to the reorientation of polymer chains at the surface to minimize surface energy.

3.3 Controlled Wettability Patterns via Combined Laser Processing and Chemical Modification

To overcome the limitation of hydrophilicity recovery and achieve stable wettability patterns, we combined femtosecond laser processing with subsequent chemical surface modifications. Initial experiments focused on creating uniform hydrophilic or hydrophobic surfaces. Oxygen plasma treatment followed by PEG-silane functionalization produced stable hydrophilic surfaces with contact angles of 15-25° that remained stable for over 30 days. Conversely, FOTS functionalization created highly hydrophobic surfaces with contact angles exceeding 150°, exhibiting superhydrophobic properties on laser-textured regions.

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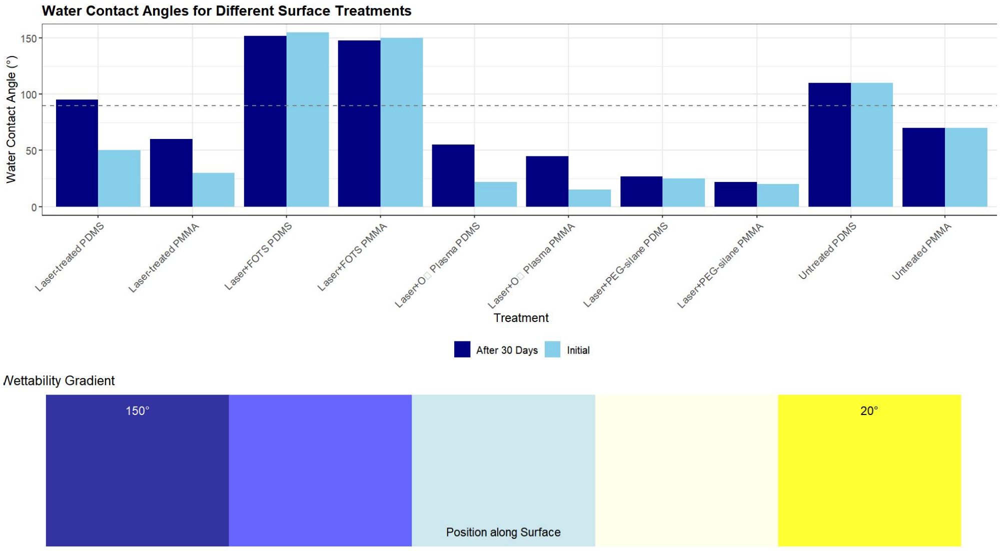

Figure 2: Surface Wettability Control via Laser Processing

The most significant achievement was the creation of spatially resolved wettability patterns with high contrast between hydrophilic and hydrophobic regionsBy first surface-treating the entire surface with FOTS to form a hydrophobic background and then employing femtosecond laser ablation for selectively etching regions to hydrophilic functionalization, we achieved wettability patterns of contrast contact angles >120°. Based on this protocol, microfluidic channels with hydrophilic inner regions surrounded by hydrophobic outer regions were feasible to prepare, hence creating conditions for the confinement of fluid within channels.

Furthermore, by controlling laser parameters and chemical modification processes, we demonstrated the ability to generate gradient wettability patterns. By modulating laser fluence across a surface and subsequently performing uniform chemical treatments, we created continuous wettability gradients with contact angles from 20° to 150°. Such gradients enable directional fluid transport under surface tension forces without the need for external energy input.

These results are in agreement with Yeo et al, who demonstrated that hydrophobic valves formed by femtosecond laser machining required a 29% pressure increase for the flow of droplets in a microchannel, while superhydrophilic valves demonstrated enhanced wettability[10].Their work demonstrated that morphological changes enhance surface roughness for hydrophobic materials but create smooth patterns for hydrophilic materials, while chemical changes were verified by FTIR and XPS measurements.

3.4 Applications in Microfluidic Devices

The methods that were created found application in the creation of functional microfluidic devices with enhanced functionality. A hydrophilic channel and hydrophobic surrounding areas Y-junction droplet generator was created that was capable of producing stable water-in-oil droplets without the incorporation of surfactants. The wettability manipulated by inhibiting wetting of aqueous phase on channel walls resulted in monodisperse droplet sizes with a coefficient of variation of

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less than 3%.
This work is particularly relevant following the recent study by Zhou et al, which demonstrated that femtosecond laser direct writing may be employed for high-precision fabrication of silica glass-based droplet generation microfluidic chips. Their study employed a combined approach of simulation, numerical calculation, and experimental validation to investigate the important parameters involved in droplet size and generation frequency, including channel wall wettability and phase flow rates.
In addition, we illustrated cell patterning ability by generating alternating hydrophilic and hydrophobic domains in a microchannel. Human endothelial cells selectively attached to hydrophilic domains modified with PEG-silane, forming sharply defined cell patterns in the absence of physical barriers. The technique holds promise for tissue engineering applications by allowing for the fabrication of complex cell patterns with just surface chemistry guidance.

4 Conclusion

This paper demonstrates the tunability of femtosecond laser processing in fabricating microfluidic chips with designed surface wettability. Through systematic investigation of the effects of laser conditions on channel morphology and surface chemistry, we established the optimal conditions for processing PDMS and PMMA substrates. The combination of laser processing and subsequent chemical post-processing enabled the achievement of long-term stable wettability patterns with good spatial resolution and contrast.Key findings include:
1. Laser fluence, scanning speed, and repetition rate significantly influence channel dimensions and quality, with optimal parameters identified for different substrate materials.
2. Femtosecond laser processing induces chemical modifications that enhance surface hydrophilicity, but these changes are temporary without additional treatment.
3. Combined laser processing and chemical functionalization enable the creation of stable wettability patterns with contact angle contrasts exceeding 120°.
4. The developed techniques can be applied to create functional microfluidic devices with enhanced capabilities for droplet generation, cell patterning, and fluid control.
Future work will focus on extending these techniques to other substrate materials, including glass and paper-based microfluidics. Additionally, we aim to explore more complex three-dimensional wettability patterns and their applications in tissue engineering and point-of-care diagnostics.

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