Plasma in Microchannel

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Without Abstract

Synonyms

Microchannel glow discharge; Microchannel surface modification; Microchannel surface sterilization; Plasma bonding

Definition

Gas plasma, a fourth state of matter, is a neutral composition of ions, electrons, radicals, and photons that is synthesized by applying energy to a gas at atmospheric pressure or within a vacuum. Gas plasma can be used to enhance the functionality of microdevices for various biological and chemical applications. The effects of plasma in microchannels are regulated by parameters such as the type of gas, power intensity, chamber pressure and duration of the treatment.

Overview

Microchannels that range in diameter from tens to hundreds of microns have emerged as potentially powerful tools for a variety of biomedical applications. They can be used to minimize sample volume and reduce costs, as well as to increase throughput and analysis sensitivity. Since microfluidic devices operate at small length scales, their functionality is greatly dependent on their surface properties, which vary depending on the type of material that is used to fabricate the channel and the subsequent surface modifications.

Microchannels have traditionally been fabricated from commonly used materials from the semiconductor industry, such as silicon. Silicon offers many advantages for microchannel fabrication, such as standardized fabrication procedures and easy integration with electronics. Despite these merits, silicon is opaque and brittle and cannot be used for fabricating transparent microfluidic devices that require light based sensors. To overcome these difficulties, glass microfluidic channels have also been developed, however, the fabrication of these devices, similar to those of silicon microchannels is time consuming, expensive and requires the use of a clean room facility. As a result, polymeric microchannels have recently emerged as potentially valuable alternatives. Polymers that have previously

been investigated for microchannels include: polycarbonate (PC), polystyrene (PS), poly(dimethylsiloxane) (PDMS) and poly(methylmethacrylate) (PMMA). One of the main advantages of using polymeric materials to make microchannels is that they can be fabricated from soft lithographic techniques such as micromolding. Furthermore, the ability to tailor the mechanical and optical properties of polymers can be used to fabricate microchannels with a wide range of properties. Despite the great advancements in the materials used to fabricate microchannels, the surface properties of these channels often require additional modifications based on the specific needs of the device. Thus, approaches to activate microchannel surfaces have been of great interest in fully realizing the potential of these techniques.

During the 1920s and 1930s, Dr. Irving Langmuir proposed the term *plasma* while he was studying the physical properties of gases and the balance of charges between ions and electrons. Commonly considered as the fourth state of matter, basic gas phase plasma contains a neutrally charged mixture of negative and positive ions, photons, electrons and radicals that are produced by applying energy to a gas at low pressure (from 10 to 10 bar). In this process, the temperature of plasma electrons is extremely high (on the order of 10 K), however, the plasma gas remains close to ambient temperature. This is because plasma components found at higher temperatures (such as the sun) are made of equilibrium (thermal) plasmas while low-pressure gas plasmas are non-equilibrium (non-thermal) type. Plasma is formed by the exposure of free electrons to an external energy source that increases the kinetic energy, resulting in the formation of radicals and ions. These excited molecules then form photoemissions, ions and free radicals due to a loss of excess energy from the plasma. The energy released from these chemical species is capable of breaking covalent bonds and altering the surface chemistry of many materials.
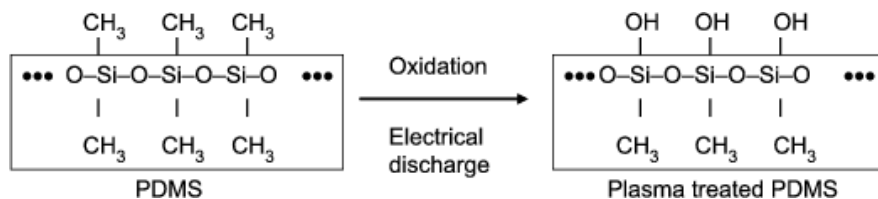

Figure 1 Schematic of the oxygen plasma treatment of a PDMS substrate

The bombardment of a surface with reactive chemical species can be used to drastically change its surface properties and create functional surfaces within microchannels. Traditionally, corona discharge and oxygen plasma treatment have been used. Corona discharge is the formation of sparks at the tip of a wire created by electromagnetic fields that result in the ionization of nearby molecules at low temperatures and pressures. Corona discharge can be used to oxidize a surface near the tip of the wire. Although widely used in various industrial processes, a negative aspect of corona discharge is its tendency to modify the surface non-uniformly. To overcome this limitation, surface plasma treatment can be used. Plasma treatment of microchannel surfaces is particularly attractive, as it does not require the tedious placement of a wire inside microscale channels. In addition, plasma treatment of a surface is faster and more reproducible compared to corona discharge.

The reaction between the plasma and a surface is highly complex and comprised of numerous and simultaneous chemical reactions [1]. Upon the initial application of energy, the gas molecules, such as oxygen, are converted to various unstable intermediates that can react with the surface. Some of the initiation mechanisms between plasma (which may include oxygen radicals) with a surface are shown below:

$$RH + O\bullet \quad \rightarrow \quad \begin{matrix} R\bullet + H\bullet + O_2 \\ R_1\bullet + R_2O\bullet \\ R\bullet + OH\bullet \end{matrix}$$
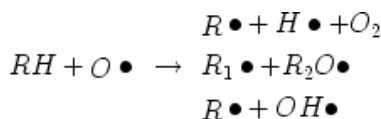
These radical species then induce chain scission, radical transfer, oxidation and disproportionation to generate functional surface groups such as hydroxyl and carboxyl moieties (Fig. 1). For some materials, such as PDMS, these activated surfaces can be bonded to fabricate channels, as shown in Fig. 2. Plasma treatment of microchannels can also be used to control surface properties by incorporating reactive molecules or by increasing the hydrophilicity of

the surfaces that eases the flow of fluids and minimizes the formation of bubbles.

In addition to adding surface functional groups, plasma can be used to remove organic contaminants and sterilize surfaces. In this process, plasma radicals break the covalent bonds and oxidize the surface contaminants, which are then cleared by the vacuum. Here, we will outline the basic methodology of gas plasma modification in microchannels, including theory, experimental methods, pertinent process parameters and characterization methods. Additionally, key research findings will be discussed.

Basic Methodology

In this section we will outline the basic methodology of the plasma treatment process. First, the theory behind plasma treatment will be presented. Following this, experimental protocol outlining the treatment process, pertinent parameters and their relevance will be discussed. Finally, surface analysis methods for plasma treated surfaces will be described, such as X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contact angle measuring tools.

Theory

To establish an analytical framework of plasma formation and initiation, thermodynamic models have been developed. For example, for low pressures and high frequencies that generate plasma gases at ambient temperatures the power required to generate plasma can be determined from molecular collision analysis. In this model, the reactive species within the plasma process are created from inelastic collisions between electrons and ground-state atoms [2], where electrons have energy, u, given by

$$u = \frac{(mw^2)}{2}$$

where w is the electron velocity and m is the electron mass. The excitation rate coefficient, C_j, of a particular species is then given by

$$C_j = \left(\frac{2}{m}\right)^{\frac{1}{2}} \int_0^\infty \sigma_j(u) F_0(u) u \, du$$

where $\sigma_j(u)$ is the particular process cross-section and F_0 is the electron energy distribution function. Nearly all processes at this level that are important possess energy threshold, u_j, where

$$\sigma_j(u) \equiv 0, \quad u \leq u_j$$

There is also a dependence of the number density $\overset{\bullet}{n}_j$ of species j produced per second in the plasma from ground state molecules (of number density $N \mathrm{cm}^{-3}$) on the electron density n, where

$$\overset{\bullet}{n}_j = C_j N n.$$

The applied electromagnetic field (where frequency $f = \omega/2\pi$) and the plasma has a power balance that is expressed by

$$P_a = \xi n V,$$

where the power absorbed is P_a, the volume of plasma is V and the average power absorbed per electron is ξ. ξ also refers to the power necessary to sustain an electron–ion pair in the plasma.

Experimental

To plasma treat a surface, samples are initially placed within a plasma vacuum chamber. Gas plasma is then generated using various energy sources such as alternating current (AC), radio frequencies (RF) or microwaves (MW) (Fig. 3). For example, in apparatuses that use RF, two electrodes apply energy in the form of magnetic and electric fields to a gas at low pressure ($\sim 266-800\,\text{mbar}$) inside the vacuum. The application of appropriate amount of energy to the gas discharge results in the formation of a neutral gas plasma. During this process, a characteristic glow is emitted from the apparatus indicating the plasma state of the gas.
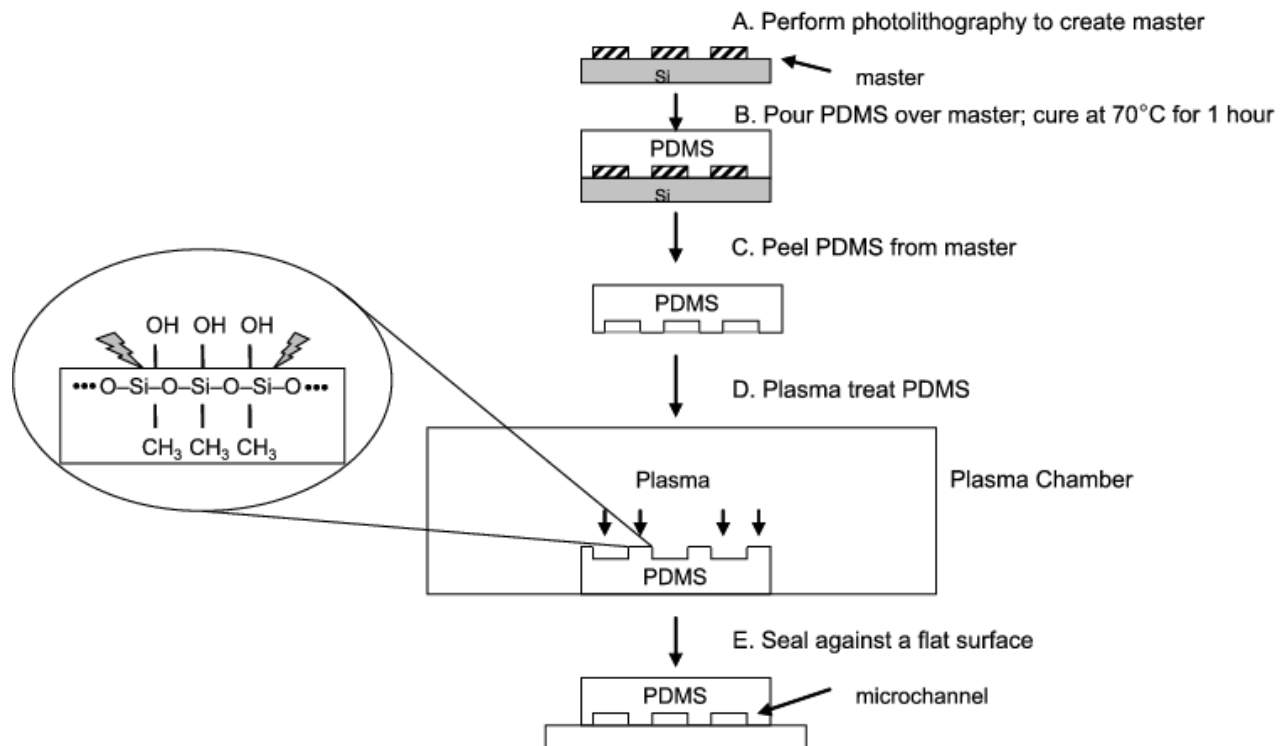

Figure 2 Schematic of the process used to fabricate microchannels through a plasma induced bonding process
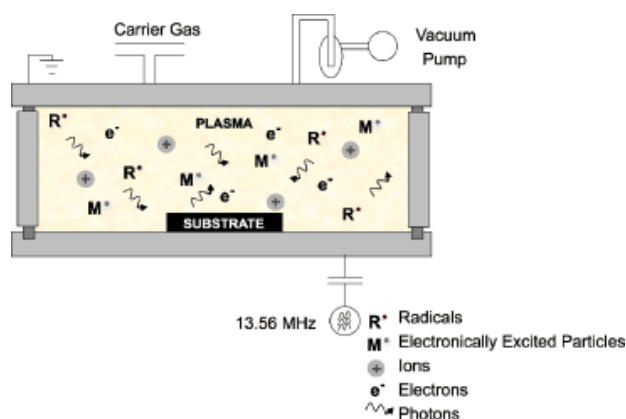
Figure 3 Schematic of a radio frequency plasma treatment chamber

Parameters

There are a number of parameters that affect the surface modification during the plasma treatment process. These parameters can be separated into internal process parameters, which are dependent on the plasma, and external process parameters, which are external to the plasma but within the system. Examples of internal parameters include the type and the degree of dissociation of the gas and the residence time of the active species in the vacuum chamber. Examples of the external parameters include, but are not limited to, the substrate material, amount of time that the material is exposed to the plasma, gas pressure, energy frequency, power and substrate temperature. It is important to note that the internal param-eters of the plasma are indirectly controlled by the external process parameters. Figure 4 depicts the relations among several parameters. This entry will discuss how the type of gas, exposure time, gas pressure and power affect the plasma initiated surface modifications and the resulting bonding strengths of substrates.

The type of gas is a key parameter in any plasma surface modification process. Plasma treatments using inert gases, such as argon, have been shown to increase the hydrophobicity of oxygen-containing polymers without adding detectable chemical species to the surface. These properties are a result of the degradation and rearrangement of molecules on the surface of the polymer. Degradation is caused by an increase in the kinetic energy in the plasma treatment chamber when inert plasmas are present. This increased energy breaks molecular bonds on the surface, which result in the degradation of the impurities on the surface of the substrate. Rearrangement of chemical species occurs as a result of cracks that are introduced onto the surface of the substrate. These cracks enable molecules from beneath to rearrange with molecules present on the surface. This is indicated by a decrease in the oxygen/carbon ratio within the treated surface, possibly resulting from loss of CO or CO_2. In contrast, plasma treatment by using

reactive gases results in the direct conjugation of the reactive molecule on the surface. For example, in the case of oxygen plasmas, hydroxyl and carboxyl functional groups are formed on the surface and can react with each other between two treated surfaces through a dehydration reaction to produce covalent linkages that result in bonding of two substrates.

The exposure time of the plasma to the surface can greatly affect its surface properties. For example, the bonding of PDMS to PDMS for the fabrication of microchannels has been shown to be time dependent (Table 1). If the substrate is not adequately treated with plasma then there will not be enough functional groups present to achieve bonding. If the substrate exposure exceeds an optimal time. Then there will be excessive oxidation of the PDMS surface and the formation, which leads to the formation of a brittle layer of silica. Thus, prolonged plasma treatment results in polymer reorganization on the substrate surface that causes decreased bonding strength due to induced hydrophobic properties.

It has also been determined that the internal pressure of the treatment chamber has a significant impact on the surface properties of treated substrates (Table 1). When the internal pressure is high, the mean free distance between molecular collisions within the plasma is significantly reduced. For example, for PDMS substrates the upper pressure

region is characterized as greater than approximately $0.1\,\mathrm{mbar}$. The molecules within this condensed plasma increasingly interact with the polymer surface molecules, resulting in increased bonding strength. Conversely, if the pressure within the chamber is too low (i. e. less than approximately $0.1\,\mathrm{mbar}$) there is reduced interaction between the plasma and the surface and the bond strength is not optimized.

Finally, power variation has also been shown to affect the surface properties of the substrate (Table 1). In the case of PDMS at low power settings, plasma electron speeds are reduced and there is less interaction between the radicals in the plasma and the substrate. This minimizes the formation of functional groups on the surface. Conversely, extreme voltages result in reduced bonding strengths because of the formation of Si–O–Si groups on the PDMS surface. The dissociation energy of these specific bonds is larger than the dissociation energy of the Si–C bonds in the backbone of the polymer, therefore causing substrate degradation and less functional group formation for PDMS-PDMS bonding. At optimal power levels the number of functional groups present on the surface of the substrate is high enough to encourage bonding but low enough to not affect the siloxane backbone of the PDMS.
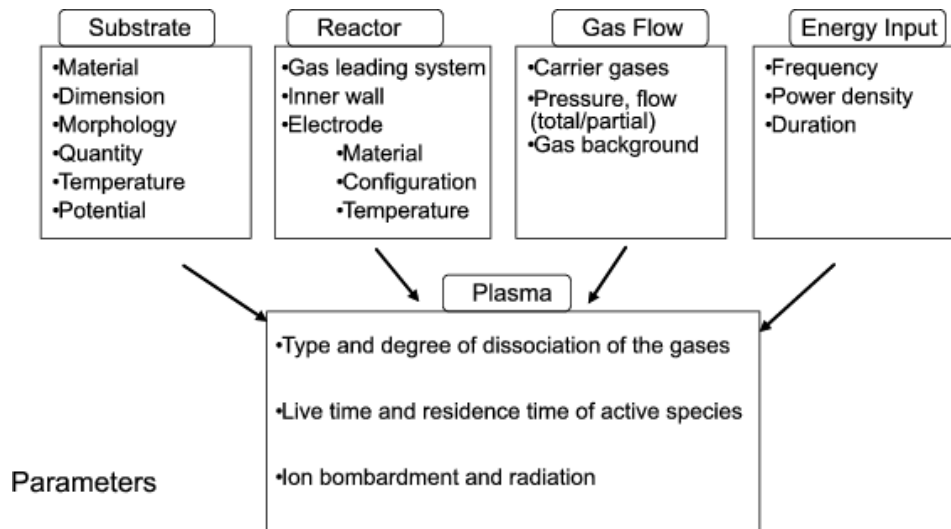

Figure 4 External parameters that influence the quality of surface plasma treatment

Table 1 Comparison of the bonding results with RIE process parameters for bonding of plasma treated surfaces. Bonding 1 metric based on permanently bonded area after immediate contact (no bonding = 0 $\sim$ whole area bonded = 10). Bonding 2 metric based on permanently bonded area when 3 days have passed after immediate contact. Adapted from [11]

#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Power (W)	70						200											300		400	500
Pressure (mTorr)	65		120		180		65		120		180		65		120		180		120		160
Time (sec)	10	40	10	40	10	40	10	40	10	40	10	40	10	40	10	40	10	40	10	40	20
Bonding 1 (max=10)	10	6	10	9	10	9	10	6	10	7	10	3	4	0	3	0	3	0	2	0	0
Bonding 2 (max=10)	10	10	10	10	10	10	10	8	10	8	10	8	4	0	3	0	3	0	2	0	0

Evaluation of Plasma Treated Surfaces

Surface chemical composition, structure and functional properties can be characterized by various techniques, such as XPS, AFM, and contact angle measurements. XPS measures the short range of photoelectrons leaving the surface. The sensitivity ($\sim 1{-}10\,\mathrm{nm}$) is semi-quantitative and detects chemical bonding information at the surface. Composition depth profiles, known as XPS spectra, can be generated from this method. Conversely, AFM utilizes a nanoscale probe to characterize surfaces and produce 3D surface profiles. AFM can determine the surface

roughness and elastic modulus through phase imaging and nanoidentations, respectively. In addition to analyzing the surface of substrates, cross-sections can be imaged by using AFM to picture the stiffer surface layer and determine thickness. Furthermore, contact angle analysis can also be used to study surface wetting behavior. Contact angle measuring devices measure the angle of a liquid–vapor interface with a solid surface to assess surface hydrophilicity. Water droplets on hydrophilic substrates spread out and have relatively low contact angle measurements. Conversely, they maintain a more spherical shape on hydrophobic substrates, thereby producing higher contact angle measurements. Common contact angle analysis methods include drop–bubble, reflective light and interference microscopy.

Key Research Findings

Various research findings on the effects of plasma treatment on microchannels have reported improved surface characteristics within microfluidic channels. Researchers have also been able to adapt plasma treatment technologies to develop novel applications in the field of engineering. Furthermore, applications of plasma in microchannels include the development of on-chip light sources and the fabrication of micropatterns and gradients for cell adhesion studies.

Hydrophobic Recovery and Bonding Enhancement Techniques

As previously mentioned, surface properties of a substrate can be tailored by applying various plasma treatments. The stability of plasma treatment is dependant on the material properties. For instance, for PDMS, oxygen plasma treated surfaces regain their hydrophobicity over time. This may be due to

- surface silanol groups reorienting into the bulk;
- movement of free PDMS chains from the bulk phase to the surface through cracks in the Si–O–Si structure;
- silanol groups at the surface condensing;
- volatile oxygen or other species escaping into the atmosphere;
- changes in the surface roughness [4].

Conversely, other explanations suggest hydrophobic recovery can be described in two distinct phases: adsorption of atmospheric contaminants and surface reorganization. Within the first few hours, the initial phase of adsorption of atmospheric contaminants begins. These atmospheric species react with the surface moieties that were introduced during treatment and reduce their functionality. In the case of PDMS, surface reorganization begins when siloxane groups from the backbone of the polymer migrate through cracks created during surface modification and reorganize to yield the original properties of the polymer. Similarly to hydrophilicity, bonding characteristics are also dependent on time (Table 2). It has been shown that the adsorption of contaminants and surface reorganization also has an adverse effect on the bonding properties of PDMS.

Table 2 Aging of activated PDMS surfaces. Bonding metric is based on permanently bonded area after aging the activated surfaces (no bonding = 0 ~ whole area bonded = 10). Adapted from [11]

#	1	2	3	4	5	6	7	8	9
Power (W)	70								
Pressure (mTorr)	75								
Etch Time (sec)	10								
Aging (min)	2	3	5	7	10	15	20	25	30
Bonding 1 (max=10)	10	10	10	10	10	10	6	7	8

To increase the stability of a surface treated substrate a variety of approaches have been developed. For example, different plasma gases can be applied to reduce the amount of surface reorganization. Specifically, nitrogen treated surfaces maintain their hydrophilicity longer than oxygen plasma treated surfaces. Also, to maintain stable

hydrophilic PDMS it is possible to fabricate C-F bonds or react poly(HEMA) bonds on PDMS microchannel surfaces [*6*].

Enhancing Microchannel Functionality

Plasma treatment of microchannels can be useful for improving the functionality of microdevices. For example, previous studies have shown that PDMS microchannels can be made hydrophilic by the addition of silane molecules with polar head groups [*7*]. In this process (3-mercaptopropyl)trimethoxysilane (3-MPS) was absorbed to PDMS to increase the hydrophilic properties of microchannels. Additionally, plasma polymerization has been used to induce in the long-term hydrophilic surface modification by covalently bonding a polymer layer to the surface. Barbier et al. [*8*] describe a method based on plasma polymerization modification with acrylic acid coatings. First, argon plasma pretreatment was used to activate trace oxygen molecules in the chamber, which partially oxidize the top layer of the substrate. This step crosslinked the surface to reduce ablation of silicon during deposition as well as limits the movement of siloxane chains for hydrophobic recovery. Secondly, plasma with acrylic acid was deposited onto the pretreated PDMS. Finally, helium plasma treatment was used to crosslink the deposited polymer film to reinforce the cohesion. This process provides a homogeneous stable hydrophilic polymer layer for robust applications within microfluidics and nanofluidics.

Applications

Applications of plasma in microchannels include the development of chromatography detectors and on-chip light sources. Evju et al. [*9*] describe the creation of microdischarges or microplasmas by direct current within microfluidic channels on polystyrene. The three different gases tested included helium (He), water-saturated helium (H_2O/He), and hexafluoroethane (C_2F_6/He). These gases were released through a microchannel and ignited at

atmospheric pressure. The treatments were completed in several seconds to reduce heat formation. XPS confirmed that oxygen and fluorine on the surfaces contributed to hydrophilic and hydrophobic regions, respectively.

Complex biomolecular micropatterns and microgradients have also been synthesized with the use of plasma treated surfaces, with possible future applications in tissue engineering, biosensors, and immunoassays. Various methodologies, such as microcontact printing and micromolding, have been used to create micropatterns where wettability was controlled through selective plasma treatment. These micropatterns are made up of many ligands and cell types for spatial control and cellular organization. This organization can induce cell–cell signaling and recreate the hierarchy lost in standard in vitro methods to produce more tissue-like structures. These advances are critical in understanding biology and enabling improved tissue culture and tissue engineering techniques.

An application of plasma treated surfaces has also been shown in microcontact printing, where elastomeric stamps are *inked* with chemical species and ligands, which can then be patterned onto different surfaces. Langowski et al. [*10*] have shown that by applying oxygen plasma to the original *stamp* there is a reduction in low-molecular-weight silicon containing fragments transferred to PMMA substrates. The effect of the treatment increased ligand bioactivity, cell function and proliferation due to reduced contamination from the initial untreated substrate. This finding allows for proper modification for applications desiring the removal of low-molecular-weigh silicon fragments, especially for biological applications.

Microgradient textures within microchannels have also been synthesized by utilizing plasma treatments. By having gradients of ligands, microchannels enable visualization of the effects on cell behavior, such as differentiation, migration and adhesion. Because of the quick and inexpensive nature of soft lithographic techniques and plasma treatments, biological applications can be done more cost effectively and in a faster manner.

Future Directions for Research

Plasma treatment of microfluidic surfaces can be used to improve microdevice functionality, to build devices through bonding processes and to activate and sterilize surfaces. Future directions for this technology include improved modeling of techniques with respect to parameter and surface plasma interaction. The development of refined

experimental methods, theoretical models, and experimental studies is required to have more control over plasma treatment within microchannels.

Cross References

Plasma Treatment Physics

Plasma Etching

AFM

Bioprinting on Chip

Cell Adhesion and Detachment

Control of Micro-Fluidics

Wetting and Spreading

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