Electroosmotic flow in vapor deposited silicon dioxide and nitride microchannels

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Electroosmotic flow was studied in thin film microchannels with silicon dioxide and silicon nitride sidewalls formed using plasma-enhanced chemical vapor deposition (PECVD). A sacrificial etching process was employed for channel fabrication allowing for cross-sections with heights of 3 μm , ranging from 2 μm to 50 μm in width. Flow rates were measured for single channels and multichannel electroosmotic pump structures for $p\text{H}$ levels ranging from 2.6 to 8.3, and zeta potentials were calculated for both silicon dioxide and silicon nitride surfaces. Flow rates as high as 0.086 $\mu\text{L}/\text{min}$ were measured for nitride multichannel pumps at applied electric fields of 300 V/mm. The surface characteristics of PECVD nitride were analyzed and compared to more well-known oxide surfaces to determine the density of amine sites compared to silanol sites. © 2007 American Institute of Physics. [DOI: [10.1063/1.2752376](https://doi.org/10.1063/1.2752376)]

I. INTRODUCTION

Microfluidic systems find increasing application in areas such as microelectromechanical systems (MEMS) sensors^{1–3} and actuators,^{4–6} biological analysis,^{7–9} and microelectronic cooling systems.^{10,11} This article considers an electrical-based fluid driving force, electrokinesis (also known as electroosmosis), that can be applied to these systems. Electroosmosis is generated due to an electric double layer (EDL) that forms when ions in a solution are attracted to charged channel walls. The strength of this attraction can be quantified by the zeta potential for a given material and solution. As an electric field is then applied along the length of the microfluidic channel, the ions that compose the shear layer of the EDL are attracted to the electrode of opposite polarity. Since the ions are solvated, they will effectively drag the solution with them, resulting in electroosmotic flow (EOF).

Several surfaces are capable of generating an EDL in the presence of a solution,^{12,13} although no surface has been studied and characterized as thoroughly as silicon dioxide. This is due to cost considerations, the ease of bulk micromachining of SiO_2 , and the large zeta potentials that SiO_2 generates within a typical $p\text{H}$ range. SiO_2 also lends itself to favorable on-channel spectroscopy due to its optical transparency, which is a very important property in most analyses. Silicon nitride is another material that has been implemented as an EDL-inducing surface.^{12,14,15} Both oxide and nitride thin films are common in microfabrication processes, where both films can be used as

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electronic insulators and passivators. Microfluidic channels based on the plasma-enhanced chemical vapor deposition (PECVD) of these films on planar substrates have recently been generated.^{16–20} PECVD is used because it allows for the formation of these films at relatively low temperatures. A large variety of materials can be coated with PECVD oxide or nitride and then be chemically removed, resulting in hollow channels. It is important to understand the electroosmotic properties of the PECVD films if these hollow channels are to be used in microfluidic systems.

This article describes EOF measurements for both PECVD silicon dioxide and silicon nitride microchannels and includes a brief review of their fabrication processes and a discussion of microfluidic structures that can be created. Zeta potentials for *pH* levels ranging from 2.6 to 8.3 for oxide and nitride channels are reported based on measured flow rates. Specific flow rates for nitride electroosmotic pump structures are also reported. Because silicon nitride surfaces have not been studied as much in the past, an analysis is made of the PECVD nitride surface that forms on the interior of the microchannels, including an extrapolation of the projected ratio of amine sites (Si-NH₂) to silanol sites (Si-OH).

II. FABRICATION

Fabrication of a thin film microchannel^{17–19} begins with a silicon or glass substrate. If a silicon wafer is used, it is necessary to first deposit a layer of thermal oxide that is approximately 3 μm thick to prevent electrical breakdown in the substrate. This is followed by 200 nm of PECVD nitride to provide an etch-stop layer to prevent the thermal oxide from being removed. The first fabrication step is depositing 300 nm of PECVD oxide or nitride at 300 °C that will act as the bottom channel wall. This is followed by thermal evaporation of a 300 nm aluminum film. AZ 3330 photoresist is then spin-coated to a thickness of 3 μm . The photoresist layer is patterned to define the microchannel cores,^{16–19} which are then reflowed on a hot plate that is ramped from 90 °C to 300 °C. This gives the channel cores a rounded shape. Next, the exposed aluminum is etched in aluminum etchant (Transene, Danvers, MA) heated to 50 °C. If the desired microchannel is oxide, a 3- μm -thick layer of PECVD oxide is applied. If the desired microchannel is nitride, a 200-nm-thick layer of PECVD oxide is applied, followed by 3 μm of PECVD oxide for structural stability. AZ 3330 photoresist is then spin-coated on the wafer surface, and the channel ends are exposed. The ends are etched in buffered oxide etch (BOE) (Transene) for approximately 8 min. The channel cores are then etched with aqua regia (2:1 HCl/HNO₃) at 80 °C for several days to remove the aluminum. The remaining photoresist core is removed with Nanostrip (Cyantek, Fremont, CA) at 50 °C for several hours.

The oxides generated using PECVD tend to match closely to most other forms of glass, although they are less dense than what could be grown in a low-pressure chemical vapor deposition (LPCVD) system or thermal furnace. The nitride layers that have been developed appear to contain few amine sites. Although the reactive gases are silane (SiH₄/He) and ammonia (NH₃), the resulting nitride thin film also appears to contain high concentrations of oxygen. Furthermore, the exact number of hydrogen atoms in each molecule of nitride is unknown, and could result in behavior that is unique to this form of PECVD nitride.

The most basic microfluidic structure is a straight, single channel. This is shown as the lower channel in Fig. 1(a). Another important microfluidic structure is the multichannel EOF pump.^{4,6,20} This is shown as the upper channel in Fig. 1(a). Any combination of these structures that can be designed on a photolithographic mask can be implemented onto a substrate. Figure 1(b) is a scanning electron micrograph (SEM) of a single oxide microchannel taken from a multichannel EOF pump, and Fig. 1(c) is an SEM of a single 50- μm -wide oxide microchannel.

III. MEASUREMENTS

Once a set of microchannels was fabricated, polymethyl methacrylate (PMMA) reservoirs were attached with epoxy over the channel openings [see Fig. 1(a)]. Pairs of 0.5-mm inner diameter Teflon tubes were embedded within each reservoir with an epoxy seal. These sets of tubing provided a buffer injection path as well as a contact point for electrodes. Measurements

FIG. 1. Microfluidic channel layout and scanning electron micrographs. (a) Illustration of a multichannel electroosmotic pump followed by a single channel, and a single channel by itself. The reservoirs placed over the channel openings are used to introduce solutions and connect electrodes. (b) SEM of a cross section of a single small oxide channel within a multichannel electroosmotic pump layout. (c) SEM of a cross section of a 50- μm -wide single oxide microchannel.

were taken by injecting a buffered solution with a syringe and marking the buffer level on each Teflon tube. Palladium electrodes were inserted through the top of the tube to the point where they were in contact with the buffer. An electric field was then applied, and the displacement of the fluid over a measured time was used to record the volumetric flow rate.²⁰ In this experiment, electrolysis was minimized by employing palladium electrodes and including hydroquinone and *p*-benzoquinone additives²¹ in the buffered solutions at a concentration of 10 mM. The electrode tips were visible during testing, and no appreciable bubble generation was witnessed for the data recorded in this paper.

An important aspect of any thin film used in microfluidic systems is understanding the effect of various *pH* levels on the zeta potential of the channel surface. If the microchannels used in this experiment are assumed to approximate to the cylindrical capillary model²² and the effects of local hydraulic resistances are ignored, electroosmotic fluid flow can be expressed by⁴

$$Q_{\text{eof}} = \frac{\pi \epsilon \zeta E d^2}{4 \eta}, \quad (1)$$

where ϵ is the electrical permittivity of the solution, ζ is the zeta potential of the microchannel inner wall, E is the electric field applied across the microchannel, d is the equivalent diameter of the microchannel, and η is the dynamic viscosity of the solution. Equation (1) can be easily rearranged to express ζ in terms of Q_{eof} . This leads to a straightforward method of calculating the zeta potential from the measured EOF. The zeta potential was measured for oxide and nitride microchannels for several electric field strengths for *pH* levels ranging from 2.6 to 8.3. The buffer concentration in each case is 10 mM, and the ionic strength of solutions falls in the range 4–30 mM. Figure 2 demonstrates the calculated zeta potentials versus buffer *pH* compared with zeta

FIG. 2. Zeta potential vs pH for PECVD silicon oxide and nitride microchannels compared against LPCVD silicon nitride (Ref. 14). For pH levels 2.6, 2.9, and 3.9, citrate buffer was used at a concentration of 10 mM at ionic strengths of 4.5, 8.7, and 22 mM, respectively. For pH levels 4.8, 6.0, 7.0, 8.0, and 8.3, phosphate buffer was used at a concentration of 10 mM at ionic strengths of 10, 12, 21, 28, and 30 mM, respectively. The LPCVD nitride curve spans a pH range from 2.4 to 6.2 with 10 mM NaCl (Ref. 14). The relative electrical permittivity was approximated to $\epsilon_r=80$ and the dynamic viscosity was approximated to $\eta=1$ mPa s. The microfluidic channels used have a width of 50 μm and height of 3 μm .

potential measurements taken by Bousse and Mostarshed for LPCVD nitride.¹⁴ Measurement error is accounted for by the error bars in Fig. 2.

Once the zeta potential for a thin film has been characterized, it is of interest to measure the flow rate that a multichannel EOF pump can produce. The top channel shown in Fig. 1(a) depicts a multichannel EOF pump. In an EOF pump, an electric field is applied across the multichannel section. This generates an EOF into the following single channel. As the fluid reaches this channel, the smaller surface area contributes little EOF, and pressurized flow dominates. This results in a back pressure through the multichannel network. For a multichannel network consisting of multiple tiny microchannels in parallel, the back pressure encounters very high hydraulic resistance. This causes most of the generated EOF to be translated into pressurized flow through the rest of the system. Pressurized flow in a cylindrical capillary can be expressed as⁴

$$Q_{\Delta p} = \frac{\pi \Delta p d^4}{128 \eta L}, \quad (2)$$

where Δp is the pressure difference across the length of the microchannel and L is the length of the microchannel. By allowing subscript 1 to refer to the tiny parallel channels and subscript 2 to refer to the single channel network that follows the pump, the total fluid flow rate in the microfluidic network can be expressed as $Q_{2,\Delta p} = Q_{1,\text{eof}} - Q_{1,\Delta p}$ (assuming that the EOF contribution in the single channel network is negligible). By substituting Eqs. (1) and (2) into this expression, Eq. (3) is obtained,²⁰

FIG. 3. Fluid flow rate vs applied electric field for nitride multichannel and single-channel EOF pump systems. The dots indicate measured points, whereas the solid lines result from values calculated using Eqs. (1) and (3). The relative electrical permittivity was approximated to $\epsilon_r=80$ and the dynamic viscosity was approximated to $\eta=1$ mPa s. The EOF pump consists of 75 channels measuring $5 \mu\text{m}$ wide and $3 \mu\text{m}$ tall each, and the remainder of the microfluidic network was $50 \mu\text{m}$ wide and $3 \mu\text{m}$ tall.

$$Q = \frac{\pi n \epsilon \zeta E L_1 d_1^2 d_2^4}{4 \eta (L_1 d_2^4 + n L_2 d_1^4)}, \quad (3)$$

where n is the number of parallel microchannels that define the EOF pump. Equation (3) represents the total fluid flow rate in a microfluidic system that employs a multichannel EOF pump. Nitride microchannels with multichannel and single-channel EOF pumps as depicted in Fig. 1(a) were tested for pH levels ranging from 6.0 to 8.0. The measured flow rates versus applied electric fields are shown in Fig. 3, compared against the flow rates calculated from Eqs. (1) and (3). The calculated flow rates were based upon the geometry of the microchannels and the calculated zeta potentials shown in Fig. 2. Since Eq. (3) represents a system with cylindrical channels, the equivalent diameter d was calculated by finding the cross-sectional channel area assuming a half-elliptical shape and solving for d as $d=2\sqrt{A/\pi}$. Flow rates as high as $0.086 \mu\text{L}/\text{min}$ were obtained for nitride multichannel EOF pumps.

IV. FILM SURFACES

When a thin film is deposited as a microchannel wall, ionized functional groups exist at the surface. These charged groups can become ionized in the presence of a solution and attract ions to form the EDL, and, consequently, the zeta potential. The chemical structure of the surface is then of great interest, since it will largely determine the EOF of a microfluidic system. Silicon dioxide is known to produce silanol sites (Si-OH) at the channel surface. Silicon nitride is known to produce primary and secondary amine sites (Si-NH₂ and Si-NH-Si) along with other possible sites, including silanol.^{11,14} Given that silanol surfaces have been measured extensively, it is illustrative to interpret the values shown in Fig. 2 to compare the theoretical ratio of amine sites to silanol

sites. This is done considering how far the zero point shifts from the oxide calculations to the nitride calculations. The ratio of amine to silanol sites can be expressed as¹⁴

$$\frac{N^{\text{NH}_2}}{N^{\text{OH}}} = 2 \sqrt{\frac{K_{a2}}{K_{a1}}} \sinh[2.303(pH_{\text{pzc}} - pH_{\text{pzc}}^{\text{OH}})], \quad (4)$$

where K_{a1} and K_{a2} are the acid dissociation constants of the silanol sites, pH_{pzc} is the zero charge point for nitride, and $pH_{\text{pzc}}^{\text{OH}}$ is the zero charge point for oxide. Bousse and Mostarshed¹⁴ have listed a typical value for the dissociation constants as $2\sqrt{K_{a2}/K_{a1}} = 7 \times 10^{-4}$. When the data represented in Fig. 2 is fit to a quadratic function and extrapolated to the respective zero charge points for the PECVD oxide and nitride, the zero charge points become $pH_{\text{pzc}} = 2.39$ and $pH_{\text{pzc}}^{\text{OH}} = 1.85$. By plugging these values into Eq. (4), $N^{\text{NH}_2}/N^{\text{OH}} = 0.11\%$. Comparing this with a value of 1.8% amine sites computed by Bousse and Mostarshed¹⁴ for LPCVD nitride, it is apparent that PECVD nitride surfaces are more highly saturated with silanol sites. Thus it seems that the majority of sites available on the nitride surface are actually silanol groups.

V. CONCLUSIONS

Thin-film microfluidic channels are fabricated using plasma-enhanced chemical vapor deposited silicon dioxide and silicon nitride. It is possible to measure the volumetric flow rates generated by electroosmosis by measuring the fluid displacement over time for an applied electric field. Zeta potentials for silicon oxide and nitride films over various pH levels were obtained through direct EOF measurement. Values as high as 0.086 $\mu\text{L}/\text{min}$ were measured for nitride multichannel EOF pumps. Thin-film silicon nitride surfaces were also evaluated and compared against silicon dioxide surfaces. It appears that silanol sites tend to dominate a nitride surface instead of amine sites. This could be due to atmospheric leakage in the PECVD vacuum system or due to a tendency for nitride surfaces to oxidize quickly. Regardless, nitride remains a powerful material for generating strong electroosmotic effects, and due to its popularity in microfabrication processes, it will likely continue to be used as a microfluidic substrate material.

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