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# The Modulation of Electrokinetic Streaming Potentials of Silicon-Based Surfaces through Plasma-Based Surface Processing

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**ABSTRACT:** A new plasma processing-based methodology for enhancing the streaming potential  $(V_s)$  that may be obtained in electrokinetic flows for a given pressure gradient over a silicon surface-based microchannel is indicated. The dependence of the  $V_s$  on both the surface zeta potential and the electrolyte slip length was carefully determined through a series of experiments involving the variation of CF4- and Ar-based plasma parameters, incorporating pressure, exposure time, and power. It was determined through analytical estimates that, while the zeta potential is always increased, the slip length may be diminished under certain conditions. A record value of ~0.1 mV/Pa was obtained using CF<sub>4</sub> plasma at 500 W, 10 mTorr, and 300 s of exposure. The implications of the work extend to the investigation of whether smooth surfaces may be effective for generating large  $V_s$ 's for new modalities of electrical voltage sources in microfluidics-based applications.

# INTRODUCTION

The generation of an electrical voltage through a pressure difference actuated flow of aqueous electrolytes is an instance of an electrokinetic phenomena that may be utilized for energy harvesting related to in situ electrical power sources in biomicrofluidics, wearable devices, better utilization of ocean scale desalination schemes, etc.<sup>1</sup> The idea of converting the kinetic energy of fluid into a continuous electrical output enables the self-power generation in a fluid system to be achieved. A major motivation then is to obtain the largest possible streaming potential  $(V_s)$  for a given pressure difference  $(\Delta P)$  across a given channel length, the efficacy of which may be defined through a figure of merit  $\left(\text{FOM} = \frac{V_s}{\Delta P}\right)$ .

Much work on harnessing the  $V_s$  through electrokinetic effects over smooth surfaces was performed by optimizing the channels. A  $V_{\rm s}$  of 40 mV was obtained through flowing a 1 mM KCl solution under a pressure difference of 3000 Pa through a glass plug with micron-scale pores of 1.0-1.6 um, corresponding to an FOM of ~0.013. Two other high-density multichannel microfluidic chips were designed and fabricated through anodic bonding and soft lithography methods, yielding a  $V_s$  of ~1200 mV (with silicon-glass channels) and ~ 800 mV

(with PDMS-glass channels) with an applied pressure difference of 1 bar.<sup>3</sup> The corresponding FOM is ~0.012 and ~0.0008, respectively. In addition to designing with multichannels, an alternate strategy is miniaturizing the device, involving the overlap of electrical double layers (EDL) to improve the  $V_s$  by facilitating unipolar ion flow. 3 V was obtained for 0.01 mM KCl in 490 nm wide silica channels under an applied pressure of 4 atm.<sup>4</sup> While in the glass nanochannel, an applied pressure of 0.35 MPa provides the  $V_s$ of about 2 V using a 10 mM KCl solution.<sup>5</sup> A major accomplishment in this regard was obtaining a greater than 2fold increase in the FOM to ~0.04 through the innovative use of a hybrid and lithographically patterned liquid filled surface (LFS).<sup>6</sup> The use of a Au nanoparticle-embedded microchannel array also obtained similar results.<sup>7</sup> In our previous work, we

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**Figure 1.** (a) A streaming potential  $(V_s)$  may be obtained in the Poiseuille flow of an electrolyte in a microchannel under the influence of a pressure gradient  $(\Delta P)$ . The related definitions of slip length (b) and surface zeta potential  $(\zeta)$  of the plasma-treated Si bottom surface  $(b_1, \zeta_1)$  and PDMS upper surface  $(b_2, \zeta_2)$  are indicated. Both (b) CF<sub>4</sub>-based and (c) Ar-based plasmas were utilized for the introduction of surface charges and modulation of the  $\zeta$ . Structural effects related to the deposit of fluorocarbon films in the case of the CF<sub>4</sub> plasma as well as the introduction of hydroxyl groups through the use of Ar<sup>+</sup> plasma, both of which diminish the effect of surface charging, must be considered in the *net* obtained  $V_s$ . (d) The  $V_s$  obtained through periodic flow of electrolyte (under a  $\Delta P$  of ~480 Pa) in the channel constituted from a *bottom surface* Si (treated with CF<sub>4</sub> plasma at 10 mTorr, 100 W, and 300 s). (e) The  $V_s$  as a function of the  $\Delta P$  for the CF<sub>4</sub> plasma-treated sample follows the H–S relation: eq 1. The figure of merit (FOM) is estimated from the slope of the  $V_s$ – $\Delta P$  plot. (f) The  $V_s$  as a function of electrolyte (aq. NaCl) concentration, i.e., 0.01, 0.1, 1, and 10 mM.

engineered the surface texture and a record number of 0.127 mV/Pa was obtained, which indicated the possibility for large potential generation.<sup>8</sup>

Generally, the magnitude of the generated  $V_s$  is critically dependent on the charge of the surface over which the flow occurs.<sup>9,10</sup> For instance, the obtained  $V_s$  is directly proportional to the zeta-potential ( $\zeta$ ), defined as the potential at the fluid slip plane, Figure 1a, through the Helmholtz-Smoluchowski (H–S) relation,<sup>11</sup> i.e.,

$$\frac{V_{\rm s}}{\Delta P} = \frac{\varepsilon}{\eta \kappa} \zeta \tag{1}$$

The  $\Delta P$  (= $P_{\rm in} - P_{\rm out}$ ) is the pressure drop across the channel, considered through the difference of the inlet pressure ( $P_{\rm in}$ ) and the outlet pressure ( $P_{\rm out}$ ). The  $\zeta$  may be positive or negative, and its magnitude is related to the surface charge density.<sup>12</sup> The properties of the electrolyte itself are considered through its dielectric permittivity:  $\varepsilon = \varepsilon_{\rm o}\varepsilon_{\rm r}$  with  $\varepsilon_{\rm o}$  being the vacuum permittivity and  $\varepsilon_{\rm r}$  being the relative permittivity;  $\eta$  is dynamic viscosity, and  $\kappa$  is electrical conductivity. With a two-dimensional surface, the electrical field extending from the surface is proportional to the surface charge ( $q_{\rm s}$ ), which may be described by the Gouy–Chapman model,<sup>13</sup> and physically implies a nonlinear decay into the electrolyte.<sup>14</sup>

The use of hydrophobic surfaces, <sup>15,16</sup> characterized through large liquid-solid contact angles ( $\theta_{CA}$ ), extends the slip length (b). The b is defined through the ratio of the velocity ( $u_s$ ) and the shear rate  $\left( = \frac{\partial u_s(z)}{\partial z} \right)$  at the surface, i.e., z = 0, i.e.,  $u_{s(z=0)} = b \frac{\partial u_s(z=0)}{\partial z}$ .<sup>17</sup> Then, the effective zeta potential  $\zeta_{eff} = \zeta \left( 1 + \frac{b}{\lambda_D} \right)$ ) may be observed and employed in eq 1 over hydrophobic surfaces<sup>6,18</sup> with  $\lambda_D$  as the Debye length, related to the extent of the double layer at the solid–electrolyte interface.

With the objective of increasing *b*, hydro-/superhydrophobic surfaces were fabricated and deployed,<sup>19</sup> e.g., mostly through the use of periodic or disordered arrays to create shear-free air pockets on solid surfaces.<sup>20,21</sup> It was proposed that the  $V_s$ increases monotonically with b until a maximum value.<sup>22</sup> Our previous experiments using textured pillar, mesh, and groove surfaces found an optimal  $V_s$  through adjusting the air fraction:  $\phi_a$  (= 1 -  $\phi_s$ ). Given the lack of surface charge in the air, the reduced  $\zeta$  offsets the contribution of the b enhancement.<sup>8</sup> Therefore, a balance of b and  $\zeta$  needs to be considered to obtain a higher  $V_s$ . Filling air gaps or infiltrating pores with liquid to form a solid-liquid composite surface was suggested as one feasible methodology to achieve such a balance.<sup>23,24</sup> In contrast to the typical air-filled surfaces (AFS), alternate liquid filled surfaces (LFS) were fabricated by replacing the air with aqueous electrolyte immiscible oil (with a finite electrical potential) and generated a larger  $V_s^{25,26}$  In such LFS, the infiltrated oil has been shown to be stable, and the LFS has been shown to maintain an intact surface over a range of pressures applied to the electrolyte flow channel.<sup>27,28</sup> It was also shown that there is negligible shear-induced drainage under external flow.<sup>29</sup> The orientational effects on such liquid filled patterned surfaces, manifested through a tensorial aspect to the developed  $V_{s}$ , were considered.<sup>28,30</sup> It was indicated through such experiments that  $\zeta$  might contribute more to  $V_s$ generation compared to the slip. In this work, we show that the surface charge density necessary for such  $\zeta$  could be provided just through plasma processing and comprises the major innovation. Our methodologies for the plasma processing of surfaces for generating a large  $V_s$  were achieved in the absence



**Figure 2.** Variations of the contact angle ( $\theta_{CA}$ ) of the CF<sub>4</sub> plasma-treated surface as a function of the (a) plasma time (power of 100 W, pressure of 10 mTorr), (b) plasma power (processing time of 300 s and pressure of 10 mTorr), and (c) plasma pressure (processing time of 300 s and power of 100 W). The  $\theta_{CA}$  of the bare/nonplasma-treated Si surface is indicated at ~65.5°. While plasma time increases the extent of hydrophobicity and the slip, both plasma power and pressure induce hydrophilicity, reducing the slip. The variation of the figure of merit (FOM), i.e., the ratio of the streaming potential ( $V_s$ ) to applied pressure difference ( $\Delta P$ ) across the microchannel constituted from CF<sub>4</sub> plasma-treated Si as the bottom surface and PDMS as the top surface. The FOM increased from ~0.04 mV/Pa (for the bare Si surface, shown as the black dot) with and increase of (d) plasma time (power of 100 W, pressure of 10 mTorr) and (e) plasma power (processing time of 300 s and pressure of 10 mTorr), while relatively remaining constant as a function of the (f) plasma pressure (processing time of 300 s and power of 100 W).

of elaborate lithographic procedures. It is a more desirable strategy and easier to implement for practical applications, related to micro/nanofluidic devices.

In this paper, we proposed the use of plasma processing of silicon (Si) surfaces to modulate b as well as  $\zeta$  related to the electrolyte flow over such surfaces. The plasma was expected to modify the related surface energies  $(\gamma)$  associated with the solid–liquid ( $\gamma_{SL})$  and the solid–air ( $\gamma_{SA})$  interfaces linked through the Young-Dupre relation, i.e.,  $\theta_{CA} = \cos^{-1} \left( \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \right)$ . A high  $\theta_{\rm CA}$  would be obtained by reducing (increasing) the  $\gamma_{\rm SA}$  $(\gamma_{\rm SL})$ . If the surface energies were thus altered, conditions related to a large b would be facilitated. The effectiveness of the plasma processing was then ascertained first through a measurement of the  $\theta_{\rm CA}$  and correlation with possible b values and then through monitoring the  $\frac{V_s}{\Delta P}$  as a figure of merit (FOM). A charge induced modulation of the surface energy could also serve to increase the  $\zeta$ . It will be shown that both an increase in the b as well as an increased effective  $\zeta$  potential may be observed. Such a modification to the H-S relation is shown to result in a larger  $V_s$  and a record FOM of 0.1 mV/Pa, 2-fold larger compared to what was previously obtained<sup>6</sup> through such experiments.

#### EXPERIMENTAL SECTION

**Fabrication of Microchannels and Patterns.** The channel for the electrolyte flow is constituted from polydimethylsiloxane (PDMS) on the top and the sides, while the plasma-treated silicon was used for the bottom surface. We report measurements on a channel of length 12 cm, width of 0.9 cm, and height of  $340 \ \mu$ m. The setup, height, and width of the channel were adjusted to ensure Poiseuille flow.

**Synthesis of Plasma-Treated Surfaces.** The Si wafers (p-type,  $\langle 110 \rangle$ , thickness of 500  $\mu$ m, from University Wafer) were cleaned by rinsing in acetone, isopropyl alcohol, and DI water successively for 60 s each. Subsequently, the native oxide of Si was removed using a 2% HF–DI water mixture at 25 °C for 60 s.<sup>31</sup> The cleaned Si was transferred into a vacuum chamber, a Reactive Ion Etching (RIE)

plasma reactor (Trion Minilock Phantom III ICP), at a temperature of 40 °C. Subsequently, plasma processing, using either  $CF_{4}$ - or argon (Ar)-based plasma, was performed immediately. The CF<sub>4</sub>-based plasmas were investigated due to the possibility of creating a thin fluorocarbon film over the surface,  $^{32,33}$  which may increase the hydrophobicity and b. However, the ions in the plasma would also have a role in removing the film, the effect of which may be exacerbated at high plasma power. The interplay of the deposition and etching of the film in a typical CF<sub>4</sub> plasma process is schematically indicated with respect to the Si surface in Figure 1b. In contrast, Arbased plasmas were considered relatively simple in terms of their constitution of a single ionized species (Ar<sup>+</sup>) and the absence of chemical reactions.<sup>34,35</sup> It was hypothesized, e.g., as indicated in Figure 1c, that the charge treated surface layer could accommodate a high concentration of stable OH<sup>-</sup> groups and yield hydrophilicity.<sup>36,37</sup> The treatment was carried out under a constant gas flow of 30 sccm and a variety of experimental conditions incorporating variations of the plasma time (in the range of 60-600 s), power (in the range of 100-500 W), and pressure (in the range of 10-100 mTorr).

Characterization of Material Surface Properties. X-ray photoelectron spectroscopy (XPS) was performed in a UHV chamber (Omicron VT, base pressure of  $5 \times 10^{-10}$  Torr) to investigate the chemical composition change of the plasma-treated surfaces. Highresolution spectra were acquired using a Mg K $\alpha$  source (h $\nu$  = 1253.6 eV) and DESA 150 electron analyzer (Staib). Analysis of the XPS data was performed using CasaXPS v2.3, and the core spectra were calibrated with a carbon correction of 284.5 eV. Atomic force microscopy (AFM; Innova, Bruker) was utilized to characterize the roughness of the surfaces. Several sample areas of dimensions 10  $\mu$ m  $\times$  10  $\mu$ m were scanned. In order to evaluate the wettability as correlated to the fluid slip, goniometry (with the Ramé-hart Model 200) was used to measure the contact angle  $(\theta_{\rm CA})$  of the electrolyte on the plasma-treated surfaces. As a reference,  $\theta_{\rm CA}$  of the HF solution treated Si surface prior to plasma processing was measured to be ~65.5°

**Streaming Potential** ( $V_s$ ) **Measurement.** Electrodes (Ag/AgCl) at either end of the microchannel were used to measure the streaming potential difference:  $V_s$ . A syringe pump (Cavro S/NxP) was used to generate the electrolyte flow, and the pressure drop ( $\Delta P$ ) along the channel length was monitored (by UEI EM152 manometer) and checked to be in correspondence with the Poiseuille characteristics



**Figure 3.** Variations of the contact angle ( $\theta_{CA}$ ) of the Ar plasma-treated surface as a function of the (a) plasma time (power of 100 W, pressure of 10 mTorr), (b) plasma power (processing time of 300 s and pressure of 10 mTorr), and (c) plasma pressure (processing time of 300 s and power of 100 W). The  $\theta_{CA}$  of the bare Si surface is indicated at ~ 65.5°. Here, plasma time and power induce hydrophilicity, reducing the slip while plasma pressure has a much smaller effect, slightly increasing the slip. The variation of the figure of merit (FOM =  $V_s/\Delta P$ ) across the microchannel constituted from Ar plasma-treated Si as the bottom surface and PDMS as the top surface. The FOM is relatively constant with (d) plasma time (power of 100 W, pressure of 10 mTorr), (e) plasma power (processing time of 300 s and pressure of 10 mTorr), and (f) plasma pressure (processing time of 300 s and power of 100 W). The FOM of ~0.04 mV/Pa was measured for the bare Si surface and shown as a black dot. The screening of the charges by the hydroxyl groups has been indicated to be responsible for the minimal modulation of the FOM.

over the chosen pressure range (150–800 Pa).  $V_{\rm s}$  was monitored six times for a given pressure difference across the channel and used to estimate the reported mean and standard deviation, as in Figure 1d. The slope of the  $V_{\rm s}-\Delta P$  plot was considered a figure of merit (FOM) and may be obtained, e.g., through Figure 1e. As a reference, the FOM of the HF solution treated Si surface, prior to plasma processing, was measured to be ~0.04 mV/Pa. Further,  $\zeta$  may be positive or negative;<sup>12,38</sup> e.g., it is typically negative for silica surfaces,<sup>12</sup> as the reported experiments were all performed at a constant pH. A decrease of the  $V_{\rm s}$  as a function of the ionic strength is indicated in Figure 1f, a general behavior that was observed in untreated as well as plasma-treated samples.

#### RESULTS AND DISCUSSION

CF<sub>4</sub> Plasma Treatment of Surfaces to Enhance the Zeta-Potential and Slip Length. The influence of the (i) time of exposure, (ii) power, and (iii) pressure related to the plasma processing on both the hydrophobicity and the electrokinetic FOM is broadly indicated in Figure 2, respectively. In each case, the other two parameters were held constant. For instance, with respect to the plasma exposure time, e.g., Figure 2a-d, the experiments were carried out at a constant pressure of 10 mTorr and power of 100 W. The pressure and the power were chosen to correspond to the conditions of maximal hydrophobicity, as determined from experiments that will be described later as inferred from Figure 2. It was then seen that the  $\theta_{CA}$  of the CF<sub>4</sub> plasma-treated Si surface increases from the native value of  $\sim 65.5^{\circ}$  to  $\sim 91.6^{\circ}$ with increased plasma exposure time. Such an increase is in accord with the expected formation of a Teflon-like film due to the exposure to  $CF_4$ .<sup>39,40</sup> Detailed XPS spectra of the (b) C, (c) O, and (d) F in CF<sub>4</sub> plasma-treated (10 mTorr, 500 W, 300 s) and untreated samples have been indicated in Figures S1 and S2 and do seem to confirm such a fluorocarbon layer, which forms after ~5 min of plasma treatment, subsequent to which there is a relative saturation of the hydrophobicity. Such observations seem to indicate a steady state related to the  $CF_4$  treatment, involving the interplay of both a deposition and etch modes;<sup>41</sup> i.e., while the film is deposited, it is simultaneously being removed as well, ultimately yielding a steady state thickness value.

In correlation to the increased hydrophobicity based on the  $\theta_{CA}$  increase by ~40%, it was determined that the FOM was augmented much more at ~112% due to the plasma exposure: Figure 2d. Such a greater increase in the FOM seems to indicate an enhanced effective zeta potential  $\zeta_{eff}$  and a significant change of the electrical properties of the Si surface. It is then plausible that there is an accumulation of electrical charges due to the CF<sub>4</sub> plasma usage, considering both the  $\theta_{CA}$  and FOM of the two samples treated for greater than 300 s.

The next set of experiments involved monitoring the  $\theta_{CA}$ and FOM as a function of plasma power (at 10 mTorr and exposure time of 300 s). Here, the degree of hydrophobicity was reduced while the FOM was increased with increasing power: Figure 2b,e, respectively. The  $\theta_{CA}$  was progressively reduced to the unprocessed Si value while the FOM was increased to a record 0.1025 mV/Pa, a factor of 2.5 larger than the bare Si. A higher plasma power is expected to bring about higher ionization in the plasma, thereby promoting the etching at the expense of the hydrophobic fluorocarbon film formation,<sup>32</sup> see Figures S1 and S2, and as also reflected in the reduced  $\theta_{CA}$ . The increased number of ions and radicals at higher power are also expected to promote surface charging and surface charge density, prompting an increase in  $\zeta$ .

The influence on the plasma pressure with a power of 100 W and treatment time of 300 s was probed next. It is generally expected that the pressure correlates inversely to the number

of ions in the plasma and, consequently, lower (higher) pressure would mimic the effects of high (low) plasma power. While  $\theta_{CA}$  was reduced with increasing pressure, Figure 2c, the FOM was relatively constant, Figure 2f. It is plausible that the dissociation of  $CF_x$  (x < 4) radicals in the plasma decreases with increasing pressure. Since the fluorocarbon film formation has been found to be well correlated to high concentrations of CF and CF<sub>2</sub> radicals,<sup>42</sup> see Figures S1 and S2, their absence would be manifested through a reduced  $\theta_{CA}$ . The absence of charged species and reduced ion interaction with the surface could also explain the lack of a change in  $\zeta$ .

In summary, the largest modulation of wettability (as inversely related to the slip length) and the FOM was obtained through the plasma time and power variables with a much less significant influence from the related pressure. A record value of the FOM indicates a profound effect with respect to  $\zeta$ , primarily obtained through the introduction of charged species into the surface. It was then hypothesized that the passive introduction of charges onto the surface would yield an enhanced  $\zeta$ . In this regard, argon-based plasmas were considered as prototypes for such aspects to be manifested.

Argon Plasma Treatment of Surfaces to Primarily Modulate the Slip Length. In a similar manner to the earlier study, the influence of the (i) time of exposure, (ii) power, and (iii) pressure, related to the Ar plasma processing on the  $\theta_{CA}$  as well as the FOM, was investigated, Figure 3. We first considered the influence of the plasma exposure time, e.g., Figure 3a,d, on experiments carried out at a constant pressure of 10 mTorr and 100 W power. It was generally observed that Ar plasma treatment reduces the  $\theta_{CA}$  without a significant change in the FOM. With respect to the former attribute, it has been reported that the Si surface treated with Ar plasma usually has more hydrophilic functional groups, e.g., hydroxyl groups, due to the formation of covalent siloxane bonds,<sup>36,37</sup> which greatly increases the wettability and yields a clue for the observed decrease of the  $\theta_{CA}$ . The influence of the surface charges is then diminished when considering such groups. While a small increase in the FOM has yet to be observed, hydrophilicity dominates. The effective roughness of the sample may be small even if the surface hydroxyl defect density is increased,<sup>34,43</sup> see Figure S3, for the related AFMbased comparison of the untreated, CF<sub>4</sub> plasma-treated, and Ar plasma-treated samples.

A similar consequence due to the plasma power was observed, Figure 3b,e. However, the increase of the plasma pressure from 10 mTorr to 100 mTorr (at a constant plasma application time of 300 s and power of 100 W) leads to a different trend, yielding a larger  $\theta_{CA}$ , Figure 3c, while the FOM seems to decrease slightly, Figure 3f. The relatively lower energy of Ar plasma at higher pressure reduces impingement onto the surface and diminishes the charge. A reduced number of OH<sup>-</sup> groups at higher plasma pressure may be one reason for the increase of the  $\theta_{CA}$ . As the surfaces are hydrophilic, the variation of effective fluid slip length would not be significant even as the  $\theta_{CA}$  increases from 25.4° to 36.3°.

In summary, Ar plasma treatment contributes substantially less to the FOM compared to that obtained using CF<sub>4</sub> plasma. However, there is far greater influence on the wettability in terms of a reduced  $\theta_{CA}$ , presumably due to the hydroxyl groups induced by the Ar<sup>+</sup> impingement. The plasma power as well as the time of plasma exposure has the greatest effect in this regard. It has been indicated that Ar<sup>+</sup> primarily sputters away O atoms in the surface SiO<sub>2</sub> yielding a Si rich surface.<sup>31</sup> The hydroxyl groups from the ambient then preferentially link to the Si and form a hydrophilic surface. The screening of the charges then detracts from any possible improvement in the  $\zeta$  and the FOM.

Correlating the Wettability to the Slip Length. It is generally expected that a higher degree of hydrophobicity (-philicity), as measured through an increased (diminished)  $\theta_{CA}$ , could be correlated with a larger (smaller) slip length, b. However, it is worth noting that determining the value, and even the order of magnitude, of b has been quite difficult. For instance, the range of b measured on microstructured surfaces through methodologies such as microparticle image velocimetry ( $\mu$ -PIV),<sup>44</sup> a pressure-drop measurement,<sup>45</sup> a surface force apparatus (SFA),<sup>46</sup> and rheometry<sup>47</sup> varies from tens of nanometers to hundreds of micrometers. Relevant to our work incorporating relatively flat plasma-treated surfaces, b would also be expected to be several orders of magnitude smaller compared to that of a microstructured surface and, hence, not amenable for accurate measurement. Consequently, we use results from computational simulations and numerical analysis, incorporating lattice Boltzmann (LB) and molecular dynamics (MD)-based methods, to associate b with  $\theta_{CA}$ . First, a relationship using the LB methodology incorporating the Shan-Chen multiphase model

$$b_{\text{S-C}} = A \times \left(e^{\theta_{\text{CA}}/B} - 1\right) \tag{2}$$

Here, *A* and *B* are fitting coefficients.<sup>48</sup> The accuracy of the fit was checked through two other relationships advocated through MD simulations,<sup>49,50</sup> i.e.,

$$b_1 \sim ([1 + \cos(\theta_{CA})])^{-2}$$
 (3a)

$$b_2 \sim (180^\circ - \theta_{\rm CA})^{-2}$$
 (3b)

A reasonable fit between all the three models, Figure 4, indicates the relative accuracy of estimating *b* through the measured  $\theta_{CA}$ . In summary, the estimated *b* after CF<sub>4</sub> plasma treatment was in the range of 0.4 to 1.2 nm, while the *b* after Ar plasma treatment does not exceed 0.3 nm. In the case of *both* CF<sub>4</sub> and Ar<sup>+</sup> plasma treatments,  $\theta_{CA}$  changes by at most



**Figure 4.** Slip length (*b*) values were estimated through a correlation of the measured contact angles ( $\theta_{CA}$ ) with the relationships obtained through computational analysis, such as the lattice Boltzmann,<sup>48</sup> see eq 2), and molecular dynamics-based<sup>49</sup> methodologies,<sup>50</sup> see eqs 3a and 3b. The *red* and the *blue* symbols are related to the use of CF<sub>4</sub>- and Ar-based plasmas, respectively. The related symbols, i.e., circle, triangle, and square, represent the variable plasma time, power, and pressure, respectively.



**Figure 5.** Estimated variation of the zeta potential ( $\zeta_1$ ) for the CF<sub>4</sub> plasma (symbols in red) and Ar plasma (symbols in blue)-treated Si surfaces as a function of (a) plasma time (power of 100 W, pressure of 10 mTorr), (b) plasma power (processing time of 300 s and pressure of 10 mTorr), and (c) plasma pressure (processing time of 300 s and power of 100 W). A  $\zeta_0$  of ~-42.7 mV, measured for an untreated Si surface, is indicated as a reference. A higher absolute value of  $\zeta_1$  was obtained using CF<sub>4</sub> plasma consistently across the parameter variation.

83°, i.e., as in Figure 2 or Figure 3, pointing to a maximum change of at most ~1.2 nm. Given that the Debye length ( $\lambda_D$ ) for a 0.1 mM NaCl concentration would be on the order of ~30 nm, the enhancement in the  $V_s$  and the FOM through the  $b/\lambda_D$  factor alone would be quite small (<5%) and in the range of error of the experimental measurement. We may then conclude that the plasma treatment has not proved adequate for increasing *b*. However, the influence of the plasma treatment on the  $\zeta$  and the FOM is much more pronounced.

Enhanced Surface Charge Density and Zeta Potential Due to Plasma Treatment. Ion impingement on the surface over a range of plasma parameters is expected to charge the surface and increase the magnitude of the surface electrical potential and the related  $\zeta$ . Applying eq 1 to the channel with averaging over the top and bottom surfaces, as previously indicated,<sup>25</sup> we obtain

$$V_{\rm s} = -\left[\frac{1}{2}\zeta_{\rm l}\left(1 + \frac{b_1}{\lambda_{\rm D}}\right) + \frac{1}{2}\zeta_2\left(1 + \frac{b_2}{\lambda_{\rm D}}\right)\right] \times \frac{\varepsilon_{\rm o}\varepsilon_{\rm r}}{\eta\kappa}\Delta P \tag{4}$$

Here,  $b_1(\zeta_1)$  and  $b_2(\zeta_2)$  corresponds to the slip length (zeta potential) of the (1) bottom plasma-treated surface and (2) the top PDMS surface, respectively. For the PDMS (with a measured  $\theta_{CA}$  of ~105°), we measured  $\zeta_2$  to be -55.5 mV using PDMS as *both* the top and bottom surfaces of the microchannel. Substituting the  $\theta_{CA}$  value into eqs 2, 3a, and 3b, we obtained a  $b_2$  in the range of 1.2–2.1 nm. An average value of  $b_2 = 1.6$  nm was then used for the slip length of PDMS. For the 0.1 mM electrolyte with  $\varepsilon_r \sim 80$ ,  $\eta \sim 0.89 \times 10^{-3}$  Pa·s, and  $\kappa \sim 10^{-3}$  S/m, we obtain a relation for  $\zeta_1$ 

$$\zeta_{1} (\text{mV}) \simeq -\frac{2514.1 \times \text{FOM} - 58.4 (\text{mV})}{1 + \frac{b_{1} (\text{nm})}{30}}$$
(5)

 $b_1$  was estimated from Figure 4 for a variety of  $\theta_{CA}$  values as appropriate for the plasma treatment, Figures 2 and 3.

The subsequent trend in  $\zeta_1$  on the Si surface with different plasma processing parameters, time, power, and pressure, under CF<sub>4</sub> (and Ar) plasma treatments are summarized in Figure 5a-c, respectively. It was seen that, (i) for all the plasma treatments reported, there was an increase in  $\zeta_1$ , (ii) a larger increase was obtained through the use of CF<sub>4</sub> plasma, and (iii) a maximum enhancement in the  $\zeta$ , i.e., by a factor of 4 (to ~-194.1 mV) compared to that of an untreated silicon surface (with a reference  $\zeta_0$  of ~-42.7 mV), was obtained at 500 W plasma power (at 10 mTorr and 300 s), Figure 5b. The 4-fold increase in  $\zeta_1$  corresponds to a 250% increase in the FOM, indicated in Figure 2e. The obtained values of  $\zeta_1$  are in agreement with previous reports.<sup>12</sup>

Article

#### CONCLUSIONS

An overarching aim of the reported work was to probe whether large values of the  $V_{\rm s}$  may be obtained on smooth, nontextured surfaces through modulation of the surface charge density. The advantage of such an approach would be that elaborate and expensive lithographic patterning could be avoided. Consequently, the use of two types of plasma  $(CF_4 \text{ and } Ar)$  and related processing parameters has been deployed. It was then determined that, while the surface charge was always increased, hence raising the absolute value of  $\zeta_1$ , structural effects related to the plasma must also be considered. For instance, in the case of the CF<sub>4</sub> plasma, the deposit of a fluorocarbon film would screen the surface charge and the reduced surface wettability of the electrolyte contributed to the  $V_s$  through an improved b. Consequently, the dual processes of surface charging and hydrophobic film deposition must be carefully controlled for an optimal  $V_s$ . Alternately, while Ar plasma may also introduce surface charges, their effect seems to be screened by the surface hydroxyl groups. Consequently, a less perceptible improvement in the  $\zeta$  and  $V_s$  was obtained. The correlation of the measured  $\theta_{CA}$  to the *b*, using computational models, was consistent with the experimental observations. However, with the estimated b < 2 nm, a  $b/\lambda_D$  enhancement contributes little to the improvement of  $V_s$  for the electrolyte concentrations reported in this work. Consequently, the major contributor to the record  $V_s$  values obtained in this study was the increased  $\zeta$ . It was then determined that the CF<sub>4</sub> plasma treatment may be tuned to yield, on average, a 50% higher  $\zeta$  compared to when Ar plasma was used. Future work would focus on plasma treatment on hydrophobic surfaces where  $\theta_{CA}$  is greater than 120° with a larger b. This would help increase both  $\zeta$  and b, yielding a higher  $V_s$  with the aim of paving the way for electrokinetic voltage sources on a larger scale. Our methodologies for the plasma processing of surfaces for generating large  $V_s$ 's are easier to implement for practical applications with immense novelty related to the self-powered nature of the associated micro/nanofluidic devices; here, external voltage sources would not be necessary, and voltage could be generated just through fluid flow.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.2c01168.

XPS-based surface analysis in plasma-treated and untreated samples; AFM-based surface characterization (PDF)

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#### Notes

The authors declare no competing financial interest.

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