Supporting Information for

Sub-10nm transparent all-around gated ambipolar ionic field effect transistor

Seung-Hyun Lee\textsuperscript{a,†}, Hyomin Lee\textsuperscript{b,c,†}, Tianguang Jin\textsuperscript{a}, Sungmin Park\textsuperscript{b}, Byung Jun Yoon\textsuperscript{c}, Gun Yong Sung\textsuperscript{d}, Ki-Bum Kim\textsuperscript{a,*} and Sung Jae Kim\textsuperscript{b,*}

1. Device fabrication

The fabrication started with bare silicon wafer (500 um thick). On top of the wafer, 1 um-thick silicon dioxide (SiO\textsubscript{2}) and 20 nm-thick amorphous Si (a-Si) was sequentially deposited (Figure 1(a)-i). Using electron beam lithography (EBL) with the e-beam resist of poly(methyl methacrylate)(PMMA), 80 nanochannels with 50 um length were patterned on a-Si (Figure 1(a)-ii). And the reactive ion etching (RIE) was followed to construct a trench structure which will be a nanochannel. That trench had 140nm width and 100 nm depth (Figure 1(a)-iii). PMMA was removed by oxygen plasma. Then, SiO\textsubscript{2} was wet anisotropically etched by Buffered Oxide Etchant (BOE) that etches only SiO\textsubscript{2}, not a-Si, resulting a circular cross-section of nanochannels (Figure 1(a)-iv). Regardless of the pattern size of a-Si (\textit{l}_{\text{RIE}} in Figure 1(a)-iv), the size of nanochannel was determined by \textit{l}_{\text{BOE}} in Figure 1(a)-iv which was fixed by the wet etch time of BOE. Because the trench width (\textit{l}_{\text{RIE}}) had a large variation due to the limitation of EBL process, this wet etch process satisfied the high reproducibility of nanochannel size. We named this process as \textit{self-limiting process}. Transparent Conducting Oxide (TCO) of Aluminum-doped Zinc Oxide (AZO) as gate electrodes was deposited 40 nm on the entire surface by Atomic Layer Deposition (ALD) (Figure 1(a)-v). Transparent AZO was used for the optical observation of substances through nanochannels, while previous work had utilized opaque metal electrodes\textsuperscript{1-5}. To prevent a leakage current through AZO electrode, we partially removed AZO at each end of nanochannel (non-gated region), remaining at the center (10 um length called gated region) (Figure 1(a)-vi). The copper
electrode pad was patterned on the contact region of AZO gate electrode using e-beam evaporator (Figure 1(a)-vii). Al2O3 dielectric oxide (70 nm thickness) was deposited on the entire surface by ALD so that a circular nanochannel with all-around-gate electrode could be formed at the center of the trench (Figure 1(a)-viii). Figure 1(b) showed schematics of fabricated nanochannel. The nanochannel had a constricted area in the middle because a gate electrode existed only at the center of nanochannel. Figure 1(c) and 1(d) showed the SEM image of the cross section of non-gated region (~100 nm opening) and gated region (~10 nm opening). After deposition of SiO2 (1.5 um thickness) on top of Al2O3 using plasma enhance chemical vapor deposition (PECVD), microchannels were fabricated near both ends of nanochannel by RIE process so that the microchannels were connected with nanochannels. The microchannels had the dimension of 60 um width and 1.5 um depth and 5 um-radius pillars were installed inside microchannel for preventing a collapse of PDMS cover as shown in Figure 1(e). Finally PDMS cover was bonded using oxygen plasma. The device was heated at 90 °C conformal bonding. Figure 1(e) showed the assembly device with magnified microscopic view near the nanochannel. Note that the color of AZO electrode (a pink color) could be observed through nanochannel array so that we confirmed the nanochannels in this work had an optical transparency.
2. Governing equations and boundary conditions

The Poisson-Nernst-Planck-Stokes formulation is valid in the system because the validity of the continuum frameworks is held down to a length scale greater than 1nm. Independent variables are electrostatic potential ($\psi$), ion concentration of $i$-th species ($c_i$), pressure ($p$), and flow field ($\mathbf{u}$) obtained by following equations,

\begin{equation}
-e_i \nabla^2 \psi = \rho_e = F \sum_i Z_i c_i, \tag{1}
\end{equation}

\begin{equation}
0 = -\nabla \cdot \mathbf{J}_i, \tag{2}
\end{equation}

\begin{equation}
\mathbf{J}_i = -D_i \nabla c_i - \frac{Z_i F D_i}{RT} c_i \nabla \psi + c_i \mathbf{u}, \tag{3}
\end{equation}

\begin{equation}
0 = -\nabla p + \eta \nabla^2 \mathbf{u} - \rho_e \nabla \psi, \tag{4}
\end{equation}

and \( \nabla \cdot \mathbf{u} = 0 \tag{5} \)

where $\varepsilon_f$ is the electrical permittivity of the electrolyte, $\rho_e$ is the volumetric charge density, $F$ is the Faraday constant, $Z_i$ is valence of $i$-th species, $D_i$ is the diffusivity of $i$-th species, $R$ is the gas constant, $T$ is the temperature, and $\eta$ is the dynamic viscosity. The Poisson equation represented by equation (1) describes the electrostatic potential distribution. The Nernst-Planck equations represented by equation (2) in which the ionic molar flux $\mathbf{J}_i$ was expressed in equation (3) describes the mass transport of charged species under consideration of the diffusion, the electromigration and the convection. The Stokes equations and continuity equation represented by equation (4) and (5) describe the fluid flow. Equations (1) ~ (5) should be solved by coupling manner.

Numerical boundaries were divided into four sections shown in Figure 2(a): dash-dot line (axis of symmetry), thick shaded (inlet/outlet), dashed line (reservoirs) and solid line (nanochannel wall), respectively. Dash-dot line represents axis of symmetry in the cylindrical coordinate system, thus this boundary possessed symmetry conditions. Thick shaded lines
denote inlet/outlet of nanofluidic system. On those boundaries, electrostatic potential, concentration, and pressure were fixed at specific values. Dashed lines indicate the boundaries of the two reservoirs on which insulating conditions were satisfied. Most importantly, solid lines denote charged walls in nanochannel on which surface charge density was set up by normal derivative of electrostatic potential and the walls had insulating condition and no-slip condition for the Nernst-Planck equations and the Stokes equations, respectively. The detailed expressions of boundary conditions were summarized in SI Table 1.

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Poisson Eq. (1)</th>
<th>Nernst-Planck Eqs. (2)</th>
<th>Stokes Eqs. (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dash-dot line</td>
<td>$\mathbf{n} \cdot \nabla \psi = 0$</td>
<td>$\mathbf{n} \cdot \mathbf{J}_i = 0$</td>
<td>$\mathbf{n} \cdot \mathbf{u} = 0$</td>
</tr>
<tr>
<td>(axis of symmetry)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thick shaded line</td>
<td>$\psi = 0$ (source)</td>
<td>$c_i = c_0$</td>
<td>$p = 0$</td>
</tr>
<tr>
<td>(inlet/outlet)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dashed line</td>
<td>$\mathbf{n} \cdot \nabla \psi = 0$</td>
<td>$\mathbf{n} \cdot \mathbf{J}_i = 0$</td>
<td>$\mathbf{n} \cdot \mathbf{u} = 0$</td>
</tr>
<tr>
<td>(reservoirs)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>solid line</td>
<td>$-\varepsilon_s \mathbf{n} \cdot \nabla \psi = \sigma_s$</td>
<td>$\mathbf{n} \cdot \mathbf{J}_i = 0$</td>
<td>$\mathbf{u} = 0$</td>
</tr>
<tr>
<td>(nanochannel wall)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$\(\mathbf{n}\) is the outward normal vector. $^bV_D$ is the applied voltage on drain electrode. $^c\sigma_s$ is the surface charge density. $^d c_0$ is the bulk electrolyte concentration.

**SI Table 1.** Boundary conditions for each equation of the model.
3. Numerical method

Numerical simulations were conducted by COMSOL 4.2, commercial FEM tool under axial-symmetric geometry and steady-state assumption. We discretized the domain into 35,000 quadrilateral elements, with finer meshes in the vicinity of the nanochannel walls. Consequently, the number of degree of freedom became ~200,000. Bulk concentration \( (c_0) \) of KCl electrolyte was in the range of \( 10^{-5} \) M to 1M and the diffusivity of each ion was \( 1.96 \times 10^{-9} \) m\(^2\)/s (\( K^+ \)) and \( 2.03 \times 10^{-9} \) m\(^2\)/s (\( Cl^- \)), respectively. The relative electric permittivity of KCl electrolyte was 80 and the dynamic viscosity of that was 0.001 Pa·s. The relative electric permittivity of Al\(_2\)O\(_3\) as oxide layer was 10 and the thickness was set to be 70 nm. We assumed the surface charge density of Al\(_2\)O\(_3\) was -1.5 mC/m\(^2\) (c.f. that of SiO\(_2\) is -2 ~ -100 mC/m\(^2\))\(^7\)-\(^10\). The assumption of negatively charged Al\(_2\)O\(_3\) was reasonable at pH 7 as our experimental condition because the point of zero charge of Al\(_2\)O\(_3\) is 6.9-10.0\(^11\). Further verification of this assumption was described in supporting information and video. Applied drain and gate voltage were in the range of -2 V to 2 V. SI Table 2 summarized the used parameters for describing a fringing field effect and a counter-ion condensation.

<table>
<thead>
<tr>
<th>( c_0 ) [M]</th>
<th>( \beta )</th>
<th>( \nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-5} )</td>
<td>20</td>
<td>0.005</td>
</tr>
<tr>
<td>( 10^{-4} )</td>
<td>200</td>
<td>0.05</td>
</tr>
<tr>
<td>( 10^{-3} )</td>
<td>2,000</td>
<td>0.5</td>
</tr>
<tr>
<td>( 10^{-2} )</td>
<td>20,000</td>
<td>2</td>
</tr>
<tr>
<td>( 10^{-1} )</td>
<td>200,000</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>2,000,000</td>
<td>2</td>
</tr>
</tbody>
</table>

**SI Table 2.** Used parameters to describe a fringing field effect and a counter-ion condensation.
4. Negatively charged Al₂O₃ at pH 7

The surface charge of nanochannel played a deterministic role for the direction of ion transportation. In this work, we covered the nanochannel surface with aluminum oxide (Al₂O₃) as a dielectric layer. While the surface charge of Al₂O₃ is usually known to be (slightly) positive, our system had a slightly negative surface charge due to its lower point-of-zero-charge than 7. To confirm the polarity, we had conducted ion concentration polarization (ICP) experiment that possessed an ion depletion zone at anodic side and an ion enrichment zone at cathodic side with negatively charged nanochannels¹². As shown in SI Figure 1, the fluorescent signal quickly disappeared at anodic side of nanochannel array to confirm that the ion depletion zone was formed at the anodic side. (Also see supporting video.) The ion depletion zone should be formed at the cathodic side if the surface charge of nanochannel was positive¹³.

SI Figure 1. The formation of the ion depletion zone at the anodic side. This confirmed that Al₂O₃ surface was negatively charged.
5. The formation of salt precipitation with high KCl concentration

After the electrical measurement with the KCl solution of concentration over $10^{-1}$M, serious salt precipitations were accumulated at the microchannel as shown in SI Figure 2. The salt precipitation decreased the cross-sectional area of microchannel so that an ionic current significantly decreased.

**SI Figure 2.** The formation of KCl precipitation after the experiment with $10^{-1}$M and 1M KCl solution.
6. Leakage current

In order to show the robustness of the system, we simultaneously measured the leakage current from source to gate. SI Figure 3 showed that the leakage currents were below 4 pA and independent from the bulk concentrations, leading to a conclusion that the leakage current would not affect on the ionic currents through source to drain. Additionally, the same order of leakage current in whole concentration range taught us that our device successfully worked without dielectric breakdown.

SI Figure 3. Leakage current as a function of drain voltage in the concentration range of $10^{-5}$ M to 1 M.
REFERENCES