Chemoreceptive Neuron MOS (CυMOS) Transistors for Environmental Monitoring: Detection in Fluid and Gas Ambients with Field Programmability and High Reliability

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Motivation

• Silicon-based autonomous microsystem
  ➢ Sensing ability
  ➢ Communication
  ➢ Computation
  ➢ Control/memory units
  ➢ Actuation capability
  ➢ Power self-sufficient
  ➢ Ease of manufacture
Outline

• CuMOS Overview
  ➢ Why – Review of literature
  ➢ What – CuMOS device structure
  ➢ How – Device operation

  ❑ Sensors
    ❑ Fluid ambient (Na⁺, K⁺, Ca²⁺, BSA and SDS)
    ❑ Gas ambient (CO₂)
    ❑ Readout circuits

  ❑ Actuators

  ➢ Conclusion
Literature Review (1/3)

• **FET-based** (Bergveld 1970)
  
  - Materials in contact with silicon oxide
  - pH sensitive
  - Many spin-offs
    - ChemFET
    - ENFET (Enzyme)
    - IMMUNOFET

Resistive-based

- Tune resistivity in the sensing scheme
- Gardner (1991)
- Lewis (1996): electronic nose
- Advantage: sensitivity from tunneling distance modulation
Literature Review (3/3)

- **Chemicapacitive**
  - Yamamoto (1987)
  - Steiner (1995)

- **Chemomechanical**
  - Grimshaw (1990)
  - Lang (1999)

- **SAW-IDT (Inter-Digital Transducers)**
  - Wenzel (1990)
  - Nakamoto (1991)

Why CuMOS?

- Integrated device structure for sensors
- Enhancement of DOFs in sensing
- Ease of integration with current CMOS technology
- Charge-based operation to reduce power consumption
- Potential for sensor-array application
- Possibility to integrated sensors and actuators with the same structure
CuMOS Objectives

• High sensitivity
• High selectivity
• Reproducibility, stability and reliability
• Simple calibration and reset protocols
• Field reconfigurability
• Versatile transient measurement
• Low power consumption in the system
• Low manufacturing cost
CωMOS Device Structure

- Extended floating gate

Only one sensing gate is used at the current stage
## Polymer-Coating Parameters

<table>
<thead>
<tr>
<th>Polymer Coating</th>
<th>Solution</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(vinyl acetate)</td>
<td>20 mg in 10 mL Tetrahydrofuran</td>
<td>90,000</td>
</tr>
<tr>
<td>poly(vinyl butyral)</td>
<td>20 mg in 10 mL Tetrahydrofuran</td>
<td>100,000–150,000</td>
</tr>
<tr>
<td>poly(ethylene -co- vinyl acetate)</td>
<td>100 mg in 10 mL Benzene</td>
<td>72:28 (wt.)</td>
</tr>
<tr>
<td>poly(vinyl chloride)</td>
<td>20 mg in 10 mL Tetrahydrofuran</td>
<td>110,000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer Coating</th>
<th>Thickness (nm)</th>
<th>Roughness Ra (nm)</th>
<th>Roughness Rq (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(vinyl acetate)</td>
<td>50</td>
<td>64</td>
<td>88</td>
</tr>
<tr>
<td>poly(vinyl butyral)</td>
<td>25</td>
<td>20</td>
<td>27</td>
</tr>
<tr>
<td>poly(ethylene -co- vinyl acetate)</td>
<td>30</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>poly(vinyl chloride)</td>
<td>30</td>
<td>8</td>
<td>13</td>
</tr>
</tbody>
</table>
Dip-Pen Technology

- For smaller sensing gates

- Molecules delivered from the AFM tip to solid substrate via capillary transport
- 30-nm linewidth resolution

Microfluidic Channels

- Close-up views
Outline

- Development of the chemoreceptive neuron MOS (C\textsubscript{ν}MOS) transistors
  - Device operations and results
    - Sensors
    - Actuators
Device Operation

• Record initial device $I-V$ characteristics
• Apply polymer coating and insulation elastomer
• Deliver fluid to the microfluidic channel (base buffer, electrolytes, or buffer loaded with protein molecules)
• Observe and record changes in threshold voltages ($V_t$) and subthreshold slopes ($S$): extract $C_{SG}$ and $\phi_{OHP}$

**Electron-tunneling operation:** apply bias ($30V$ or $-30V$ for 50 seconds) at the control gate

• Observe and record $V_t$ and $S$
• Perform cleansing steps (e.g. rinsing, $N_2$ drying)
• Re-align insulation layer and repeat $I-V$ measurements
Phenomena at the Interface

• GCS model

$$C_{EDL} = \frac{1}{C_H} + \frac{1}{C_{DIF}}$$

$$C_H = \int_0^{A_{SG}} \left( \frac{\varepsilon_r \varepsilon_0}{x_{OHP}} \right) dA$$

$$C_{DIF} = \int_0^{A_{SG}} \left( \frac{2\varepsilon_r \varepsilon_0 z^2 q^2 n}{kT} \right)^{1/2} \cosh \left( \frac{zq\phi_{OHP}}{2kT} \right) dA$$

- $z$: magnitude of the charge on the ions
- $n$: concentration of the ions
- $\phi_{OHP}$: potential at the OHP
Capacitive-Divider Model

\[ I = I_0 e^{kV_{FG}/U_T} \left( e^{-V_S/U_T} - e^{-V_D/U_T} \right) \]

\[ \kappa = C_{ox}/(C_{ox} + C_{dep}) \]

\[ V_{FG} = \frac{Q}{C_T} + \frac{C_{gs}}{C_T} V_S + \frac{C_{gd}}{C_T} V_D + \frac{C_{CG}}{C_T} V_{CG} + \frac{C_{SG}}{C_T} V_{SG} \]

\[ \Delta V_T = -\frac{Q}{C_T} - \frac{C_{gs}}{C_T} V_S - \frac{C_{gd}}{C_T} V_D \]

\[ C_T = (C_{ox} \parallel C_{dep}) + C_b + C_{gs} + C_{gd} + C_{CG} + C_{SG} \]

Subthreshold current model

Above-threshold voltage-shift model

Changed by fluids
Notations:

c : after applying insulation elastomer with microfluidic channels

m : after delivering the sample fluid

o : after tunneling electrons out of the floating gate

t : after cleansing steps and a period of time in the dry box with constant N₂ flow
Sensing-Gate Responses

• Influence from the fluid
  - Induce image charge at the extended floating gate
  - Modify series capacitance to the sensing gate
  - Affect floating-gate potential and total capacitive load; create distinctive threshold-voltage shifts and subthreshold-slope variations

• Capacitance indication
  - Collect information via capacitive coupling from the fluid bulk to the extended floating-gate structure
  - Detect variations before and after electron-tunneling operations
Subthreshold Slopes

\[ C_T = \left( C_{\text{ox}} / C_{\text{dep}} \right) + C_b + C_{gs} + C_{gd} + C_{CG} - C_{SG} \]

\[ V_{FG} = \frac{Q}{C_T} + \frac{C_{gs}}{C_T} V_S + \frac{C_{gd}}{C_T} V_D + \frac{C_{CG}}{C_T} V_{CG} + \frac{C_{SG}}{C_T} V_{SG} \]

\[ I = I_0 e^{\kappa V_{FG}/U_T} \left( e^{-V_S/U_T} - e^{-V_D/U_T} \right) \]

\[ S \equiv \left[ \frac{\partial (\log_{10} I)}{\partial V_{CG}} \right]^{-1} \]

\[ S = \frac{U_T \ln 10}{\kappa} \left( \frac{C_T}{C_{CG}} \right) \]

Extraction of \( S \) values

DI Water on Polysilicon

Drain Current (A)

Control Gate Voltage (V)
Data Analyses

• Extraction of subthreshold slopes from the measured I-V recordings
• Direct estimation of sensing-gate capacitance ($C_{SG}$), eliminating control-gate capacitance ($C_{CG}$) variation

\[
C_T = (\beta S) C_{CG} \\
C_T = C_p + C_{CG} + C_{SG} \\
C_p = \left(\frac{\beta S - 1}{\beta S_r - 1}\right) \left( C_{SGr} + C_{pr} \right) - C_p \\
\beta = \kappa / (U_T \ln 10)
\]
**Reference $S_r$**

<table>
<thead>
<tr>
<th></th>
<th>$d_{1r}$</th>
<th>$d_{1c}$</th>
<th>$d_{1m}$</th>
<th>$d_{1i}$</th>
<th>$d_{1t}$</th>
<th>$d_{2r}$</th>
<th>$d_{2c}$</th>
<th>$d_{2m}$</th>
<th>$d_{2i}$</th>
<th>$d_{2t}$</th>
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</thead>
<tbody>
<tr>
<td>5 mM KCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>polysilicon</td>
<td>148</td>
<td>177</td>
<td>553</td>
<td>728</td>
<td>166</td>
<td><strong>200</strong></td>
<td>213</td>
<td>771</td>
<td>1019</td>
<td>217</td>
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<tr>
<td>poly(vinyl acetate)</td>
<td><strong>187</strong></td>
<td>198</td>
<td>270</td>
<td>272</td>
<td>194</td>
<td><strong>284</strong></td>
<td>296</td>
<td>435</td>
<td>455</td>
<td>293</td>
</tr>
<tr>
<td>poly(vinyl butyral)</td>
<td><strong>228</strong></td>
<td>231</td>
<td>687</td>
<td>985</td>
<td>228</td>
<td><strong>160</strong></td>
<td>176</td>
<td>663</td>
<td>830</td>
<td>165</td>
</tr>
<tr>
<td>poly(ethylene -co- vinyl acetate)</td>
<td><strong>163</strong></td>
<td>197</td>
<td>673</td>
<td>711</td>
<td>180</td>
<td><strong>156</strong></td>
<td>183</td>
<td>575</td>
<td>668</td>
<td>166</td>
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<tr>
<td>poly(vinyl chloride)</td>
<td><strong>288</strong></td>
<td>301</td>
<td>469</td>
<td>491</td>
<td>279</td>
<td><strong>212</strong></td>
<td>215</td>
<td>1164</td>
<td>1308</td>
<td>219</td>
</tr>
</tbody>
</table>

**Notations:**

- $d_{1}, d_{2}$: device 1, device 2
- $r$: initial reference
- $c$: after channel formation
- $m$: after fluid delivery
- $i$: electron tunneling in, 30 V, 50 s.
- $t$: recordings after cleansing steps and a period of time in the dry box

Normalization required to get rid of the fabrication variation
Normalized $\Delta C_{SG}$

**Before electron tunneling**

**Sample Fluids**

- DI water
- 0.005M NaCl
- 0.005M KCl

- polysilicon
- poly(vinyl acetate)
- poly(vinyl butyral)
- poly(ethylene -co- vinyl acetate)
- poly(vinyl chloride)

**After electron tunneling**

**Sample Fluids**

- DI water
- 0.005M NaCl
- 0.005M KCl

- polysilicon
- poly(vinyl acetate)
- poly(vinyl butyral)
- poly(ethylene -co- vinyl acetate)
- poly(vinyl chloride)

**Before electron injection**

- Variation by polymers (√)
- Difference between fluids (X)

**After electron injection**

- "Discernible patterns"
Selectivity Demonstration (1/2)

Before electron injection
“Difference not obvious”

After electron injection
“Discernible patterns”

Mixture contains both solutions in corresponding concentration
Selectivity Demonstration (2/2)

- Sensor-array plots

Additive or subtractive responses in the sensor-array plots
### Double-Layer Parameters (1/3)

**ΔC_{diff} from extracted S**

<table>
<thead>
<tr>
<th>ΔC_{diff} (µF/cm²)</th>
<th>DI Water</th>
<th>NaCl Solution</th>
<th>KCl Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50µM</td>
<td>0.005M</td>
<td>0.05M</td>
</tr>
<tr>
<td>polysilicon</td>
<td>6.4</td>
<td>7.0</td>
<td>7.5</td>
</tr>
<tr>
<td>poly(vinyl acetate)</td>
<td><strong>20.1</strong></td>
<td>1.7</td>
<td>7.5</td>
</tr>
<tr>
<td>poly(vinyl butyral)</td>
<td>1.8</td>
<td>6.0</td>
<td>13.2</td>
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<tr>
<td>poly(ethylene -co-vinyl acetate)</td>
<td>1.2</td>
<td>8.9</td>
<td>67.7</td>
</tr>
<tr>
<td>poly(vinyl chloride)</td>
<td>1.1</td>
<td>2.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>

\[
S = \frac{U_T \ln 10}{\kappa} \left( \frac{C_T}{C_{CG}} \right) \\
C_{SG} = \left( \frac{\beta S - 1}{\beta S_r - 1} \right) \left( C_{SGr} + C_{pr} \right) - C_p \\
\beta = \frac{\kappa}{U_T \ln 10}
\]
Double-Layer Parameters (2/3)

- Extracted $\phi_{OHP}$ (before elec. injection)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\phi_{OHP}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005M</td>
<td></td>
</tr>
<tr>
<td>0.05M</td>
<td></td>
</tr>
<tr>
<td>0.5M</td>
<td></td>
</tr>
<tr>
<td>50µM</td>
<td></td>
</tr>
<tr>
<td>500µM</td>
<td></td>
</tr>
<tr>
<td>DI water</td>
<td></td>
</tr>
</tbody>
</table>

Slope $\approx 60$ mV/decade

Nernst Equation

$$E = E_0 + \frac{RT}{nF} \ln \left( \frac{C_{Ox}}{C_{Rd}} \right)$$

$Ox + ne \leftrightarrow Rd$

$RT/F = kT/q$

$\approx 25.9$ mV at room temp.

$\phi_{OHP}$ decreases at $\approx 60$ mV/dec. with increases in concentration
Double-Layer Parameters (3/3)

\[ \Delta \phi_{OHP} \] (after electron injection)

\[ \begin{align*}
\Delta \phi_{OHP} & \quad \text{(mV)} \\
\text{Concentration} & \\
\text{DI water} & \quad 0 \quad 20 \quad 40 \quad 60 \quad 80 \quad 100 \quad 120 \\
\text{NaCl} & \quad \text{Surface: Polysilicon} \\
\text{KCl} & \\
\text{DI Water} & \\
\end{align*} \]

\[ \begin{align*}
\Delta \phi_{OHP} & \quad \text{(mV)} \\
\text{Concentration} & \\
\text{DI water} & \quad 0 \quad 20 \quad 40 \quad 60 \quad 80 \quad 100 \quad 120 \\
\text{NaCl} & \quad \text{Surface: Poly(vinyl butyral)} \\
\text{KCl} & \\
\text{DI Water} & \\
\end{align*} \]

The change of the \( \phi_{OHP} \) increases with increasing concentration in NaCl.

For KCl solution, no significant increasing trend is observed as in NaCl.
Detection in Gas Ambients

CO₂ on Polysilicon

Control Gate Voltage (V)

Drain Current (A)

ΔV_{to}

ΔV_{ti}
Protein Sensing

Gate Voltage (V)

Drain Current (A)

SDS (Uncharged)
SDS (Charged)
BSA (Uncharged)
BSA (Charged)
Lysozyme (Uncharged)
Lysozyme (Charged)

BSA: bovine serum albumin
SDS: sodium dodecyl sulfate
\[ \Delta V_d = \frac{2U_T}{\kappa} \frac{C_T}{C_{CG1}} \ln \left( \frac{e^{\frac{I_{in}}{I_s}} - 1}{e^{\frac{I_{in}}{I_s}} - 1} \right) \]

\[ \propto S \left( \frac{\ln10U_T}{\kappa} \frac{C_T}{C_{CG1}} \right) \]

**CMOS Circuit Integration**

MOSIS AMI foundry fabrication (April 2004)

Current mirrors

Control/clock

DC bias current for power/freq tradeoffs

Sample and hold

**CMOS Circuit**

RTD biasing

Current mirrors

Sample and hold

V_s readout

V_d readout
Sample-and-Hold Control Signal

Control signal for sample and hold in the readout circuits (monitoring signals from measurement)
Readout Calibration

Quasi-static operations with reliable resets
Readout Channel

![Graph showing Readout Channel performance with water and 2 μM KCl solutions.](image)
Outline

- Development of the chemoreceptive neuron MOS (CνMOS) transistors
  - Device operations and results
    - Sensors
    - Actuators
Electrowetting Actuation

- Conventional approach – the change of surface tension at the solid-liquid interface by directly applying different voltages

- Young’s equation
  \[ \gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta \]

- Lippman’s equation
  \[ \gamma_{sl} = \gamma_{sl0} - \frac{C_{edl}}{2} (V - V_0)^2 \]

\[ \theta = \arccos \left( \cos \theta_0 + \frac{C_{edl}}{2\gamma_{lg}} (V - V_0)^2 \right) \]
Device Structures

Microfluidic channel only partially covered to avoid air pressure against actuation

Transparent elastomer layer provides easy observation of the saline-water actuation
Equilibrium in the Channel

- Interface
- IHP
- OHP
- Specific Adsorbed Ion
- Solvated Ions
- Solvent molecule
- Diffuse Layer

Air

γ_g

θ

γ_sg

γ_sl

Solid
Actuation Scheme

- Fluid Reservoir
- Aligned insulation
- Elastomer layer

- Source
- Drain
- Control gates

- Floating-gate extension
- Drain
- Source
- Drain
- Source
- Drain
Result Illustrations

Device Type 1

Before electron injection

Channel width 20µm

Empty channel segment (no liquid)

After electron injection

~10µm

Liquid front advancing

Metal connection to reference voltage

Device Type 2

Before electron injection

Actuation surface

Embedded active area for reference voltage

After electron injection

Floating gate underneath actuation surface

~5µm

Trapped air bubble

Liquid front advances about 10 µm after electrons are tunneled to the floating gate

Less change in equilibrium liquid length for the wider channel after actuation
Control Experiments

Control test #1
- Liquid front advancing by directly sweeping external voltages
- Liquid front advancing ~10μm
- Channel width 20μm
- Connection to ramping voltage
- Connection to ground

Control test #2
- Unaltered liquid front
- Initial condition
- After 30 minutes

Asymmetrical liquid-front advancing by directly sweeping external voltages

Equilibrium length of the liquid almost unchanged after 30 minutes
Electrowetting on CvMOS

- Modification of interfacial charges results in the change in solid-liquid interfacial tension and hence the equilibrium length of the liquid in the microfluidic channel
- Potential for integration with the CvMOS sensors and conventional CMOS circuitry for fluid delivery
- Air-trapping considerations for further device designs in microfluidic application
- No actuation observed for KCl solution; results agree with $\Delta \phi_{OHP}$ after elec. injection
Selective to Buffer Species

$\Delta \phi_{OHP}$ (after electron injection)

The change of the $\phi_{OHP}$ increases with increasing concentration in NaCl.

For KCl solution, no significant increasing trend is observed as in NaCl.
Smart Sensors and Actuators

- Controlled fluid delivery for more reliable sensing
- Analysis/feedback circuitry from CMOS to provide fluid information (variety, position, etc.)
- Various surface coatings individually applied on sensors and/or actuators
Outline

• Development of the chemoreceptive neuron MOS (CνMOS) transistors
  - Why – Review of literature
  - What – CνMOS device structure
  - How – Device operation
    - Sensors
    - Actuators

• Summary and future directions
• FET devices with extended floating gates for chemical sensing
• Floating-gate structure for electron-tunneling operations provides more DOFs for sensing
• Indicators from I-V characteristics: Subthreshold slopes ($S$) and threshold voltages ($V_t$)
• CMOS integration enables detailed control circuits
Summary (2/2)

• Normalized $\Delta C_{SG}$ in the polymeric responses directly couples to subthreshold slopes and the patterns encourage sensor-array application in the lock-and-key implementation.

• Electrowetting actuator for potential microvalves integrated with the sensors and conventional CMOS circuitry for fluid delivery and confinement.