SUPPORTING INFORMATION

Correlation of Low-Frequency Noise to the Dynamic Properties of the Sensing Surface in Electrolytes

Da Zhang,[†] Paul Solomon,[*,§] Shi-Li Zhang,[†] and Zhen Zhang[*,†]

[†]Solid-State Electronics, The Ångström Laboratory, Uppsala University, SE-751 21 Uppsala, Sweden, and [§]IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, US.

This material includes:

1. Evaluation of static properties a_S, C_{Stern}, and N_S,

2. Simplified expression of τ_p, R_s, and R_p,

3. Dependence of f_c on surface properties,

as well as the following figures:

Figure S1. *p*H sensivity depicted as function of binding site density N_S with varying C_{stern} at *p*H=7,

Figure S2. Equivalent circuit of the site-binding impedance z_{SB}.

Corresponding authors:

* E-mail: solomonp@us.ibm.com

* E-mail: zhen.zhang@angstrom.uu.se

1. Evaluation of static properties a_S, C_{Stern}, and N_S

The variation of φ_S with that of *p*H, i.e. $\Delta\varphi_S/\Delta p\mathrm{H}$, is commonly defined as the sensitivity for the ISFETs, quantification of which has been well addressed by the site-binding model[1]. To conquer the complexity of the original site-binding model, van Hal el. develop a general approach[2] to calculate the *p*H sensitivity, where, a key parameter is the surface H^+ buffer capacitance C_{buff}. Introduction of C_{buff} brings a concise but physically meaningful expression for the *p*H sensitivity S_{pH} as follow[2]:

$$S_{pH} = \frac{\Delta\varphi_s}{\Delta p\mathrm{H}} = \frac{59.2\ \mathrm{mV}/p\mathrm{H}}{\frac{C_{DL}}{C_{buff}} + 1} \tag{S1}$$

where, φ_S denotes the surface potential, and C_{DL} the EDL capacitance. The calculations of C_{DL} and C_{buff} depend on the EDL model and charging mechanism applied, respectively. In the present work, C_{DL} is calculated via Gouy-Chapman-Stern model, in which C_{DL} is the series connection of Stern capacitance C_{Stern} and the diffuse layer capacitance C_{diff}. On the other hand, C_{buff} is accounted for by the original Yates el.'s site-binding charge mechanism[2], and calculated with:

$$C_{buff} = \frac{\mathrm{d}\sigma_0}{\mathrm{d}\varphi_S} = \frac{q^2 N_S}{kT}\frac{D_2 K_B a_S}{D_1^2} \tag{S2}$$

where, σ_0 denotes the surface charge density, q the elementary charge, N_S the density of surface OH group, k Boltzmann constant, T the temperature, a_S surface H^+ concentration, $D_1 = K_A K_B + K_B a_S + a_S^2$, and $D_2 = K_A K_B + 4K_A a_S + a_S^2$. Using eqs. S1 and S2 with a measured S_{pH}, a_S, C_{Stern}, and N_S can be solved implicitly, provided value of any of three parameters is known.

C_{Stern}, with its nature taken into account, is determined by the structure of electrolyte and interfacial charging condition[3], rather than the surface structure; therefore, it should be considerably similar, and thus assigned with the same value for the samples at a certain *p*H value in our modelling,. In Figure S1, S_{M} is depicted a function of N_{S} at *p*H=7. In our modeling, C_{Stern} was searched within the reported range[2] from 0.2 to 1.4 Fm^{-2}. To achieve a good fitting of S_{V}^{n} to the measurement and a reasonable value compared to the reported ones[2], C_{Stern} was assigned as 0.34 Fm^{-2}, corresponding to the solid line in the figure, and the values of the derived N_{S} for the samples, depicted in the figure too, are listed in table 1 in the main text, where S_{M}, K_{A} and K_{B} can also be found. Since the measured sensitivity S_{M} for the three samples is different, the derived N_{S} can be considerable variable for the samples too, as shown in the figure, which may arise from the uneven morphology and structure of the ALD oxide film at its early growth stage.

2. Simplified expression of τ_{p}, R_{s}, and R_{p}

The site-binding impedance z_{SB} can be decomposed to a sum of first-order partial fractions:

$$z_{\text{SB}} = \frac{1}{y_{\text{SB}}} = \frac{1}{sC_{\text{buff}}} + \frac{R_{\text{p}}}{1+s\tau_{\text{p}}} + R_{\text{s}} \tag{S3}$$

where, buffer capacitance C_{buff}, resistances R_{s} and R_{p} and time constant $\tau_{\text{p}} = R_{\text{p}}C_{\text{re}}$ are associated with the site-binding reactions. They expressions have been detailed in our recent work[4]. Here we utilize $K_{\text{B}} \gg a_{\text{S}} \gg K_{\text{A}}$ and $K_{\text{B}}K_{\text{A}} \approx a_{\text{S}}^2$ to further simplify their expressions, as follows:

$$C_{\text{buff}} = \frac{q^2 N_{\text{S}}}{kT}\frac{D_2 K_{\text{B}} a_{\text{S}}}{D_1^2} \approx \frac{q^2 N_{\text{S}}}{kT}\frac{2a_{\text{S}}}{K_{\text{B}}} \tag{S4a}$$

$$\tau_{\mathrm{p}} = R_{\mathrm{p}} C_{\mathrm{re}} = \frac{1}{D_2}\left(\frac{a_{\mathrm{S}}}{c_{\mathrm{A}}} + \frac{K_{\mathrm{A}}}{c_{\mathrm{B}}}\right) \approx \frac{1}{D_2}\frac{K_{\mathrm{A}}}{c_{\mathrm{B}}} \approx \frac{1}{2K_{\mathrm{B}}c_{\mathrm{B}}} \tag{S4b}$$

$$R_{\mathrm{s}} = \frac{kT}{q^2 N_{\mathrm{S}}}\frac{D_1}{K_{\mathrm{B}}a_{\mathrm{S}}(a_{\mathrm{S}}c_{\mathrm{B}} + K_{\mathrm{A}}c_{\mathrm{A}})} \approx \frac{kT}{q^2 N_{\mathrm{S}}}\frac{1}{K_{\mathrm{A}}c_{\mathrm{A}}} \tag{S4c}$$

$$\begin{aligned} R_{\mathrm{p}} &= R_{\mathrm{s}}\frac{a_{\mathrm{S}}K_{\mathrm{A}}\left[a_{\mathrm{S}}(c_{\mathrm{A}} - 2c_{\mathrm{B}}) + K_{\mathrm{A}}(2c_{\mathrm{A}} - c_{\mathrm{B}})\right]^2}{D_2^2 c_{\mathrm{A}}c_{\mathrm{B}}} \\ &\approx \frac{kT}{q^2 N_{\mathrm{S}}}\frac{D_1}{K_{\mathrm{B}}K_{\mathrm{A}}a_{\mathrm{S}}c_{\mathrm{A}}}\frac{a_{\mathrm{S}}K_{\mathrm{A}}(a_{\mathrm{S}} + 2K_{\mathrm{A}})^2 c_{\mathrm{A}}^2}{D_2^2 c_{\mathrm{A}}c_{\mathrm{B}}} \approx \frac{kT}{q^2 N_{\mathrm{S}}}\frac{D_1 a_{\mathrm{S}}^2}{D_2^2 K_{\mathrm{B}}}\frac{1}{c_{\mathrm{B}}} \\ &\approx \frac{kT}{q^2 N_{\mathrm{S}}}\frac{1}{a_{\mathrm{S}}c_{\mathrm{B}}} \end{aligned} \tag{S4d}$$

$$C_{\mathrm{re}} = \frac{\tau_{\mathrm{p}}}{R_{\mathrm{p}}} \approx \frac{q^2 N_{\mathrm{S}}}{kT}\frac{2a_{\mathrm{S}}}{K_{\mathrm{B}}} \tag{S4e}$$

3. Dependence of f_{c} on surface properties

The site-binding z_{SB} can be described with the equivalent circuit depicted in Figure S2. From the expressions of all the components in the circuit as formulated with eqs S4a-e, it can be found that

$$C_{\mathrm{buff}} = C_{\mathrm{re}} \tag{S5a}$$

$$R_{\mathrm{p}} \gg R_{\mathrm{s}}\text{, in the limit of } c_{\mathrm{A}} \gg c_{\mathrm{B}} \tag{S5b}$$

Therefore, the circuit can be approximated with the $½C_{\mathrm{buff}} - R_{\mathrm{s}}$ branch since the two capacitors are in series. The comer frequency f_{c} of the branch, i.e. f_{c} of the site-binding network, is found as:

$$f_{\mathrm{c}} = \frac{1}{2\pi R_{\mathrm{s}} C_{\mathrm{buff}}/2} = \frac{K_{\mathrm{A}}K_{\mathrm{B}}c_{\mathrm{A}}}{2\pi a_{\mathrm{S}}} \approx \frac{a_{\mathrm{S}}c_{\mathrm{A}}}{2\pi} \tag{S6}$$

Figures

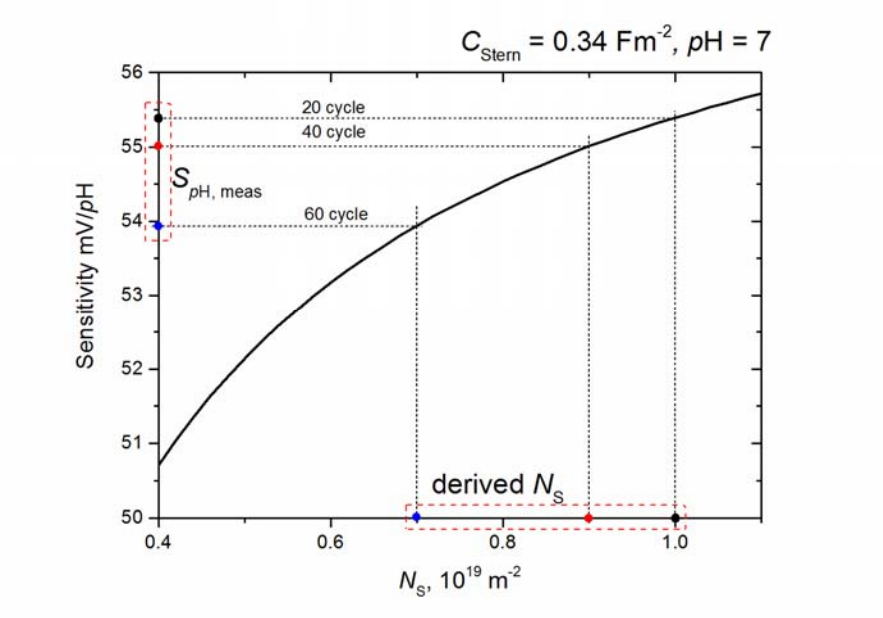

Figure S1. *p*H sensivity depicted as function of binding site density N_S with varying C_{stern} at *p*H=7.

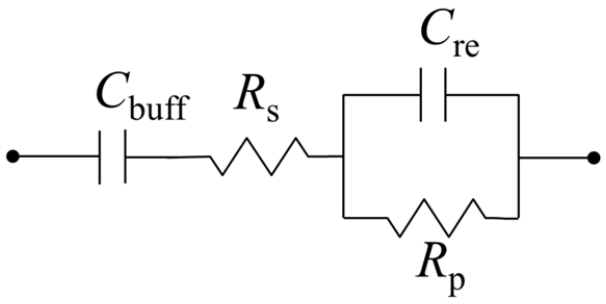

Figure S2. Equivalent circuit of the site-binding impedance z_{SB}.

Reference

(1) Yates, D. E.; Levine, S.; Healy, T. W. Site-Binding Model of the Electrical Double Layer at the Oxide/water Interface. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1974**, *70* (0), 1807.

(2) van Hal, R. E. G.; Eijkel, J. C. T.; Bergveld, P. A General Model to Describe the Electrostatic Potential at Electrolyte Oxide Interfaces. *Adv. Colloid Interface Sci.* **1996**, *69* (1–3), 31–62.

(3) Brown, M. A.; Goel, A.; Abbas, Z. Effect of Electrolyte Concentration on the Stern Layer Thickness at a Charged Interface. *Angew. Chemie - Int. Ed.* **2016**, *55* (11), 3790–3794.

(4) Zhang, D.; Solomon, P.; Zhang, S. L.; Zhang, Z. An impedance model for the low-frequency noise originating from the dynamic hydrogen ion reactivity at the solid/liquid interface. Sens. Actuators, B 2017, 1 DOI: 10.1016/j.snb.2017.07.054.