

Towards Electro-Chemical Gating by CMOS

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Abstract:

Electrolyte-oxide-semiconductor (EOS) capacitors were fabricated to elucidate; (a) the dynamics of the ionic double layer under field-effect modulation, (b) the effect of electrolyte composition on the zero-field voltage, and (c) the role of insulator surface groups on the differential capacitance of the fluidic double layer. Surface groups, owing to their amphoteric nature, are known to regulate charge when a potential is applied, which in turn sets up the double layer at the solid-electrolyte surface [1]. Through this study, we show a complex interplay between double layer dynamics, ionic composition and surface groups through capacitance-voltage measurements. Valency of the cationic species was shown to result in a strong hysteretic effect dependent on surface charge density. Varying time intervals during the cyclic sweep indicated the dynamics of ionic adsorption/desorption effects. The potential of hydrogen (pH) dependence was shown to exhibit near-Nernstian sensitivity. The pH response increased for increase in surface charge density, indicating that ionic adsorption might play the additional role in determining the zero-field potential.

Introduction:

Electro-fluidic gating is an effect where an applied field imparts control over the ionic layer on an electrolyte/solid interface, called the electric double layer [1]. Fields emanating

from buried electrodes in solution are usually screened by counterions over a characteristic length, termed the Debye length. Beyond this length scale, Coulomb forces exerted on molecules are negligible. Recently the chemical nature of the interface was found to play a profound effect on charge modulation.

Through this study, we aimed to understand how the electrofluidic gating effect changed with different interface chemistries. We performed the study using simple EOS capacitors (Figure 1) with different dielectric layers.

Experimental Procedure:

The fabrication process consisted of three splits. The first split had 30 nm of thermally grown silicon dioxide (SiO_2) deposited on a clean Si wafer followed by a patterning to open up the capacitor areas. Positive photoresist SPR 220 3.0 was used and exposure was done by ABM contact aligner. A descum was carried out for 10s in the Oxford 82 etcher. The second process split included various oxide layers deposited on the Si wafers by the atomic layer deposition (ALD) tool, including hafnium oxide (HfO_2), tantalum oxide (Ta_2O_5), aluminum oxide (Al_2O_3) and SiO_2 interfaces. The third process split included 20 nm of thermally grown SiO_2 on a metal-oxide-semiconducting (MOS) cleaned Si wafer, followed by 70 nm of n^+ polysilicon.

The wafers were then spun with SPR 220 (3.0) and exposed through the ABM contact aligner. The YES Image Reversal oven was employed to change the tone of the photoresist from positive to negative. After development, the wafers were CHF_3/O_2 etched in the Oxford 82 etcher, leaving blocks of polysilicon on the wafer. After stripping off the photoresist, 200 nm layer of silicon nitride (Si_3N_4) was deposited on the wafer to serve as the passivation layer. A subsequent photolithography step was performed to open up the capacitor active area. An RIE etch was performed to remove any residual resist. The wafers consisted of capacitors of three different sizes ranging from $300 \mu\text{m} \times 300 \mu\text{m}$ to $1000 \mu\text{m} \times 1000 \mu\text{m}$. Capacitance versus voltage (CV) measurements were made on the devices with the Keithley 4200 semiconductor characterization system.

Here we report measurements with the largest capacitor.

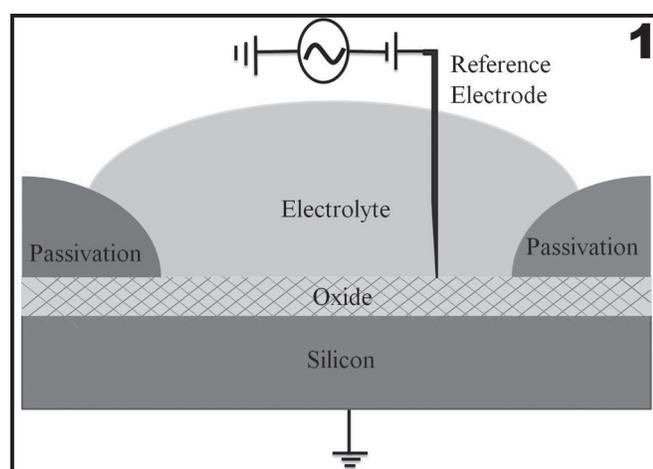


Figure 1: The EOS capacitor device.

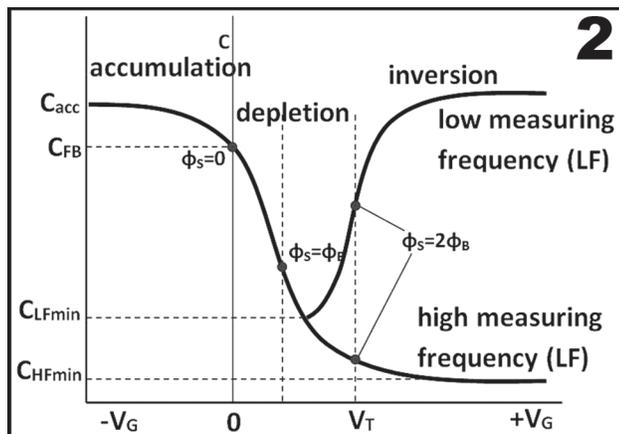


Figure 2: Typical MOS capacitor CV behavior.

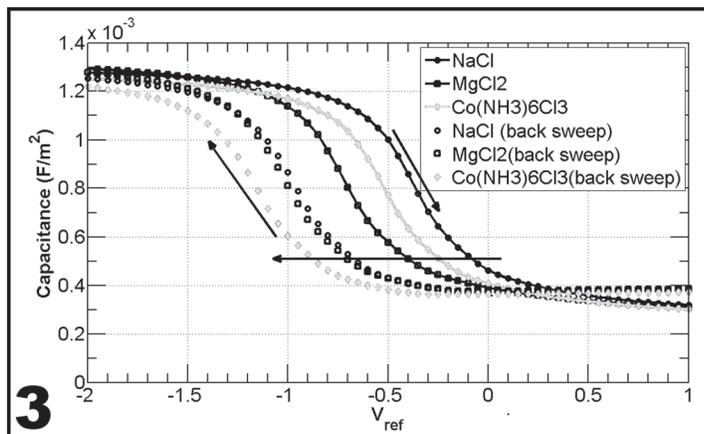


Figure 3: Cation valency comparison on polysilicon capacitors performed at pH 7.

Results and Conclusions:

CV measurements reported here were carried out on three different surfaces consisting of; (a) polysilicon, (b) Al_2O_3 , and (c) thermal SiO_2 . Behavior of a typical MOS capacitor is shown in Figure 2. The inversion characteristic of a MOS capacitor is a strong function of applied frequency. Exceeding a cutoff frequency, originally mobile charges (either electrons at the silicon interface or ions at the electrolyte-solid interface) will stop responding to the AC excitation and behave like a simple dielectric layer, which decreases the overall capacitance. We chose a frequency where ions continued to respond while electrons at the silicon interface did not. A frequency of 5 kHz was used to perform our measurements.

Comparison of pH. The capacitors were tested with 20 mmol sodium chloride (NaCl) electrolyte of pH 3, pH 5, pH 7, pH 9 and pH 11. With decreasing pH, the zero-field voltage shift reduced, indicating a larger positive charge adsorption to the interface. As the pH reduced, the number of H^+ ions increased, modulating the charge in silicon. For polysilicon, Al_2O_3 and thermal SiO_2 , the flat-band voltage, as a function of pH, showed a clear 50 mV/pH response, which was in line with Nernstian theory. The pH response was found to be higher however as the surface charge density increased.

Concentration Comparison. We tested four different concentrations of NaCl (0.1 mmol, 1 mmol, 20 mmol and 100 mmol) to evaluate how the zero-field voltage changed as a function of electrolyte concentration. It was observed that with increasing concentration, the capacitance in the accumulation region increased primarily due the double layer capacitance, but the zero-field voltage remained more or less constant within ± 50 mV. We attribute this to screening-limited response where the interface acted like a buffer.

Cation Valency Comparison. We tested EOS capacitors using 20 mmol NaCl, MgCl_2 and $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ to assess the effect of cation valency on the behavior of the double layer. It was observed that with increasing valency both the accumulation capacitance and the zero-field voltage lowered.

The decrease in zero-field voltage was also different for higher valency ions.

A large hysteric effect was observed on both polysilicon and Al_2O_3 capacitors. We attributed this to ion-specific effects, which were caused by large density of surface sites and roughness. The positive sweep (-2V to 2V) implied a large density of negative charge accumulation at the oxide interface, while on the return it indicated the opposite (cation adsorption). This excess positive charge led to a memory effect at the interface due to differential desorption rates.

Future Work:

Various effects such as ion size and ion-ion correlations need to be included to understand the interface behavior further with complex electrolytes.

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References:

- [1] Jiang, Z.; Stein, D. Electrofluidic Gating of a Chemically Reactive Surface. *Langmuir* 2010, 26, (11), 8161-8173.