

Single atomic layer ferroelectric on silicon

Supporting Information

Mehmet Dogan^{1,2}, Stéphanie Fernandez-Peña^{1,3}, Lior Kornblum^{1,4}, Yichen Jia^{1,5}, Divine P. Kumah^{1,4}, James W. Reiner^{1,4}, Zoran Krivokapic⁶, Alexie M. Kolpak⁷, Sohrab Ismail-Beigi^{1,2,4,8}, Charles H. Ahn^{1,2,4,8} and Frederick J. Walker^{1,4*}

¹Center for Research on Interface Structures and Phenomena (CRISP), Yale University, New Haven, CT 06520, USA

²Department of Physics, Yale University, New Haven, CT 06520, USA

³Department of Quantum Matter Physics, Université de Genève, Genève 1211, Switzerland

⁴Department of Applied Physics, Yale University, New Haven, CT 06520, USA

⁵Department of Electrical Engineering, Yale University, New Haven, CT 06520, USA

⁶GLOBALFOUNDRIES, Santa Clara, CA 95054, USA

⁷Dept. of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

⁸Department of Mechanical Engineering and Materials Science, Yale University, New Haven, CT 06520, USA

*fred.walker@yale.edu

Polarization of the ferroelectric ZrO₂

In order to find the polarization of the ZrO₂, we compute the shift in the flat band voltage between the Pt/Al₂O₃ (12 nm)/Si and Pt/Al₂O₃ (22 nm)/ZrO₂ (1 nm)/Si systems. The flat band capacitance (per area) is given by¹

$$C_{FB} = \left(\frac{1}{C_{ox}} + \sqrt{\frac{k_B T}{e^2 \epsilon_S (N_a - N_d)}} \right)^{-1}, \quad (1)$$

where $C_{ox} = \frac{\epsilon_{ox}}{d_{ox}}$ is the capacitance of the oxide, ϵ_S is the dielectric constant of the semiconductor substrate, and N_a and N_d are acceptor and donor densities in the semiconductor, respectively.

To estimate the flatband voltage for the Pt/Al₂O₃/Si system, we use $\epsilon_{ox} = \epsilon_{Al_2O_3} \cong 10\epsilon_0^2$, $d_{ox} = d_{Al_2O_3} = 12 \text{ nm}$, $T = 300 \text{ K}$, $N_a \cong 6 \times 10^{15} \text{ cm}^{-3}$ and $N_d \cong 0$. This yields $\frac{C_{FB}}{C_{ox}} \cong 0.2$. Using this value and the C-V data in Figure 3 we estimate $V_{FB} \cong 1.5 \text{ V}$.

For the most general case of a metal/oxide/semiconductor system that includes charge accumulation at the oxide/semiconductor interface and a non-zero charge density inside the oxide, the flat band voltage is given by

$$V_{FB} = \phi_M - \phi_S - \frac{1}{\epsilon_{ox}} \int_0^{t_{ox}} \rho_{ox}(x) x dx - \frac{P_{ZrO_2} d_{ZrO_2}}{\epsilon_{ZrO_2}}, \quad (2)$$

where $\phi_M - \phi_S$ is the work function difference between the metal and the semiconductor, $\frac{1}{\epsilon_{ox}} \int_0^{t_{ox}} \rho_{ox}(x) x dx$ is the voltage drop across the oxide due to the spatial charge density in the oxide, and $\frac{P_{ZrO_2} d_{ZrO_2}}{\epsilon_{ZrO_2}}$ is the voltage drop across the oxide due to the polarization at the oxide/semiconductor interface. For a p-type semiconductor

$$\phi_S = \chi + \frac{E_g}{2} + k_B T \ln \frac{N_a}{n_i}, \quad (3)$$

where $\chi = 4.05 \text{ eV}$ is the Si electron affinity³, $E_g = 1.14 \text{ eV}$ is the Si band gap³, $N_a \cong 6 \times 10^{15} \text{ cm}^{-3}$ and $n_i \cong 1.5 \times 10^{10} \text{ cm}^{-3}$ are the acceptor density and the intrinsic carrier density in doped Si, respectively. This yields $\phi_S = 4.96 \text{ eV}$. Given $\phi_M = \phi_{Pt} = 6.35 \text{ eV}$ ³, we find $\phi_M - \phi_S \cong 1.4 \text{ eV}$. This value is close to the $V_{FB} \cong 1.5 \text{ V}$ value that we find via the C-V curve. Therefore the contributions of the second and the third terms in Eq. (2) are small, leading us to conclude that no significant surface or volume charges accumulate in Al_2O_3 .

We repeat the calculation of V_{FB} from the C-V curve for the Pt/ Al_2O_3 / ZrO_2 /Si system, $C_{ox} = \left(\frac{d_{\text{Al}_2\text{O}_3}}{\varepsilon_{\text{Al}_2\text{O}_3}} + \frac{d_{\text{ZrO}_2}}{\varepsilon_{\text{ZrO}_2}} \right)^{-1}$, where $d_{\text{Al}_2\text{O}_3} = 22 \text{ nm}$, $d_{\text{ZrO}_2} \cong 1 \text{ nm}$ and $\varepsilon_{\text{ZrO}_2} \cong 20\varepsilon_0$ ⁴. This yields $\frac{C_{FB}}{C_{ox}} \cong 0.3$. Inspecting the C-V curve in Figure 3 for this system, we estimate $V_{FB}^{(\uparrow)} \cong 0.8 \text{ V}$ and $V_{FB}^{(\downarrow)} \cong 0.4 \text{ V}$.

These values are much smaller than the $V_{FB} \cong 1.4 \text{ V}$ we find for the Pt/ Al_2O_3 /Si system. In Eq. (2) the first two terms only depend on the metal and the semiconductor, and thus this difference should be due to the last two terms. We find that there is no significant charge in the Al_2O_3 , and since the deposition method is the same with and without ML ZrO_2 , we do not find trapped charge in the Al_2O_3 for the Pt/ Al_2O_3 / ZrO_2 /Si system. The shifts are attributed to the surface polarization density of the ML ZrO_2 layer, since we expect the spatial charge density in ZrO_2 to be negligible. Using d_{ZrO_2} and $\varepsilon_{\text{ZrO}_2}$ from above and Eq. (2), we find $P_{\text{ZrO}_2}^{(\uparrow)} \cong 12.4 \mu\text{C}/\text{cm}^2$ and $P_{\text{ZrO}_2}^{(\downarrow)} \cong 19.4 \mu\text{C}/\text{cm}^2$. Both cases have a positive sign for the ZrO_2 polarization at the interface with Si, which indicates that the majority of the dipoles point downward in both polarization states.

Composition at interface

Figure S1 shows a superposition of energy dispersive x-ray spectroscopy (EDX) line profiles over a raw scanning-transmission electron microscopy (STEM) micrograph. The line profiles were calculated from a 2D EDX map by summing the intensity along the vertical pixel column of the EDX map, across the entire image height shown in Fig. S1. The image and elemental map were acquired simultaneously. An insignificant misalignment of several pixels (1 pixel = 0.019 nm) is possible during the plotting process. From the Si intensity profile we estimate the spatial resolution to be in the order of 2 nm, and within this resolution we estimate that the ZrO_2 layer is positioned between the silicon and Al_2O_3 layer.

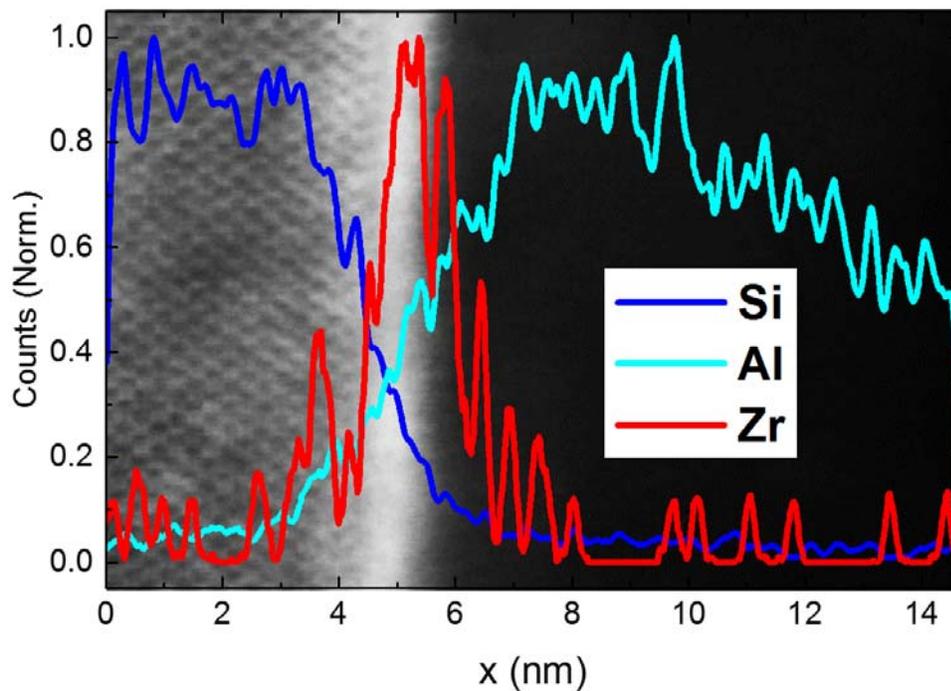


Figure S1. Superposition of a high-resolution STEM image and EDX intensity profiles of Si, Al and Zr. The profiles are calculated from by summing the intensities through the entire height of the image.

References

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