

Direct Evaluation of SiO₂/Al₂O₃ Interface Dipole for Si/SiO₂/Al₂O₃/HfO₂ Gate Stack Using Operando HAXPES

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Background Dipole techniques have been investigated to control the threshold voltage (V_t) in n- and p-FETs, and Al₂O₃ has been proposed as a candidate dipole material for p-FETs [1,2]. An Al₂O₃ dipole layer is inserted at the SiO₂/HfO₂ interface of Si/SiO₂/HfO₂ gate stacks, and its thickness is controlled by the number of atomic layer deposition (ALD) cycles. V_t is known to be affected by both fixed charges and dipoles in the gate stack; however, it has been difficult to separate them by electrical measurements. In this study, we directly evaluate the SiO₂/Al₂O₃ interface dipole in Si/SiO₂/Al₂O₃/HfO₂ stacks using hard X-ray photoelectron spectroscopy under gate bias (operando HAXPES) [3].

Experiment Al/p-Si/SiO₂(9 nm)/Al₂O₃(0 or 0.2 nm)/HfO₂(4 nm)/Pt stacks were prepared using ALD. Using operando HAXPES at SPring-8 BL46XU ($h\nu = 7.94$ keV, $|V_g| \leq 1.5$ V), Hf 3d, Si 1s and Pt 3d spectra were acquired while applying a gate voltage [Fig. 1(a)]. As each core level follows its layer's potential, $\text{sep}_c = \text{BE}(\text{Si } 1s (\text{Si}^{4+})) - \text{BE}(\text{Hf } 3d_{5/2})$ gives the HfO₂–SiO₂ potential difference across Al₂O₃. The measured interface dipole was corrected as sep_c reflects only 60% of the actual value due to a 40% V_g drop between Hf 3d and Si⁴⁺.

Results The Al₂O₃-induced change in sep_c was 0.14 ± 0.03 eV after correction for the V_g drop [Fig. 1(b)]. This actual interface dipole was independent of V_g and polarity [Fig. 1(b),(c)], excluding the possible influence of mobile ions and charge trapping. The sep_c of the 0.4-nm-thick Al₂O₃ sample was almost the same due to saturation of the dipole effect (data not shown). Both the corrected sep_c value and saturation trend are consistent with reported C–V results (V_{fb} shift of +0.14 to +0.25 V) [4]. Thus, operando HAXPES is a promising analysis method to evaluate the SiO₂/Al₂O₃ interface dipole under gate bias.

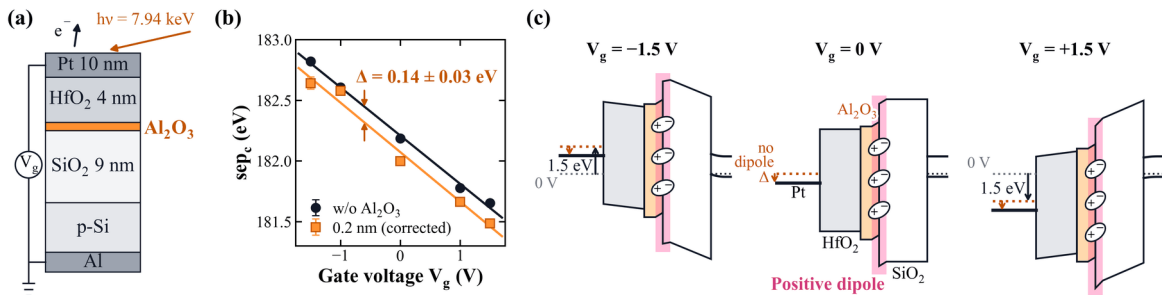


Fig. 1 (a) Illustration of sample and setup. (b) Corrected sep_c – V_g plot. (c) Schematic band diagrams.

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Supplementary Pages

S1. Definition of sep_c . Figure S1 shows the Si 1s and Hf 3d spectra of the 0.2-nm-thick Al_2O_3 sample (2 cycles of ALD) at $V_g = 0$ V. Each peak position was determined by fitting each spectrum with Voigt profiles after Shirley background subtraction. The measured sep_c was calculated from the difference in peak positions between Si 1s (Si^{4+}) and Hf 3d $_{5/2}$.

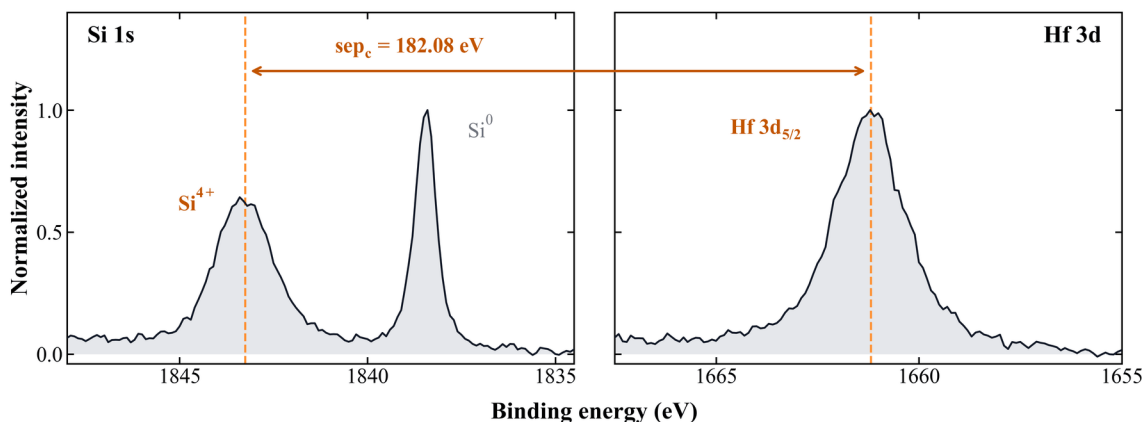


Fig. S1 Si 1s and Hf 3d spectra of the 0.2-nm-thick Al_2O_3 sample (2 cycles of ALD) at $V_g = 0$ V.

S2. Bias partition. Figure S2 shows the shift of each core level with V_g . From the slopes, 40% of V_g drops between Hf 3d and Si 1s (Si^{4+}) in both samples, which gives the slope of sep_c (-0.40 eV/V).

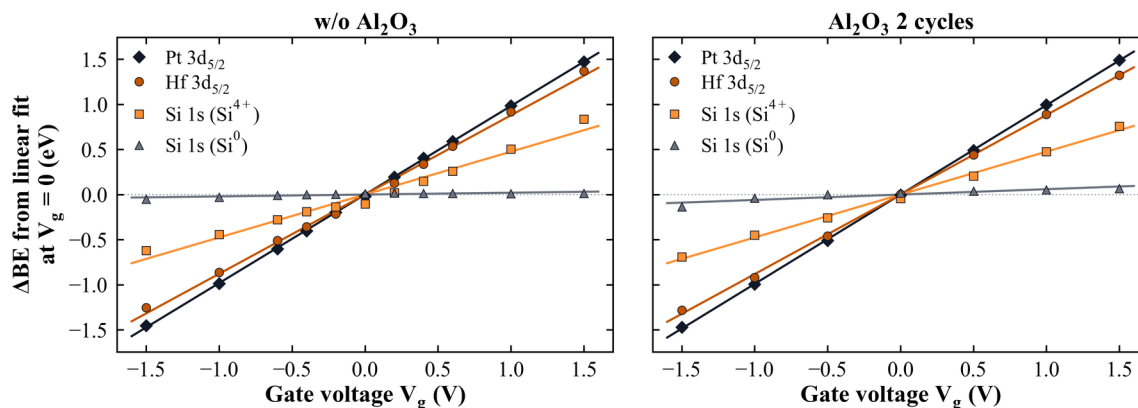


Fig. S2 $\Delta\text{BE}-V_g$ plots of each core level for the samples w/o Al_2O_3 (0 cycle of ALD) and with 0.2-nm-thick Al_2O_3 (2 cycles of ALD), relative to the linear fit at 0 V.

S3. Compensation of an interface dipole under a gate bias. Figure S3 shows how the dipole is compensated. A 0.2-nm-thick Al_2O_3 film (2 cycles of ALD) forms an interface dipole Δ at the $\text{SiO}_2/\text{Al}_2\text{O}_3$ interface (Fig. S3(b)). In this state, sep_c changes by Δ since only the energy levels of HfO_2 and Pt drop by Δ . Because Pt and Si are connected to the voltage source, Pt is pulled back to 0 V ($V_g = 0$) (Fig. S3(c)). From Fig. S2, 40% of this voltage (Δ) drops between Hf 3d and Si 1s (Si^{4+}), indicating that sep_c recovers 40% of Δ . The change in sep_c is therefore only 60% of the dipole: the measured shift of 0.086 eV is corrected to an actual dipole of $\Delta = 0.086/0.60 = 0.14$ eV. The uncertainty of ± 0.03 eV comes mainly from the standard error of this shift over the five V_g values measured for both samples (± 0.018 eV), divided by 0.60.

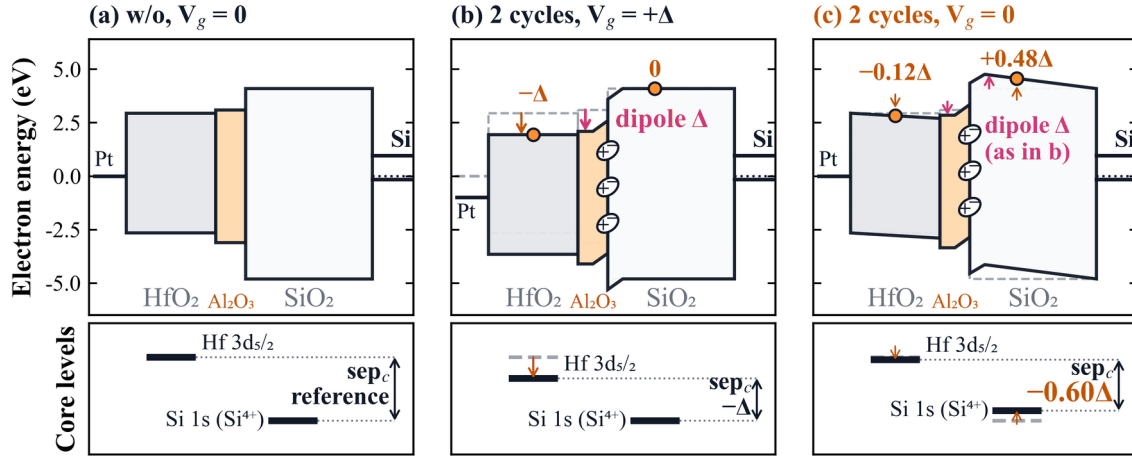


Fig. S3 Schematics of the dipole compensation in the band diagrams and core levels (dipole exaggerated to 1 eV).

S4. Precision of the peak positions. Figure S4 shows the V_g dependence of sep_c for the sample w/o Al_2O_3 . The dashed line is a least-squares fit to the nine data points. Since 40% of V_g drops between Hf 3d and Si^{4+} (Fig. S2), sep_c shifts by about 0.08 eV per 0.2 V step (measured: 0.06–0.10 eV). The residuals from this line (lower panel) have an RMS of 0.012 eV, so the measurement precision of sep_c is about 0.01 eV. This precision is sufficient for discussing differences of several tens of meV.

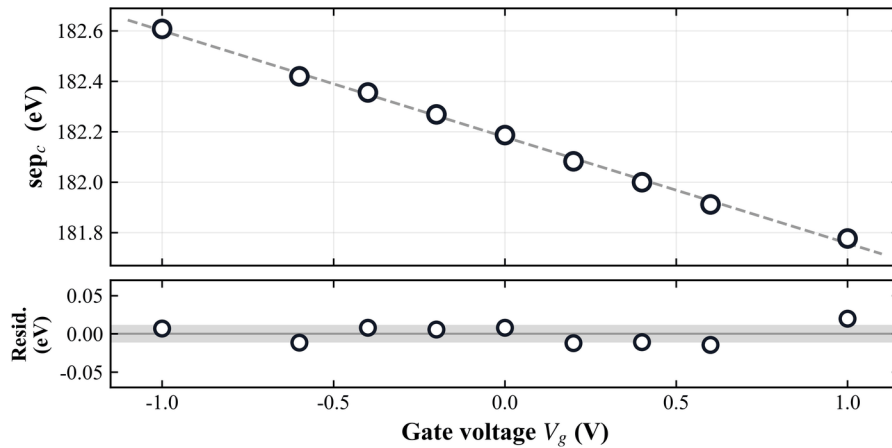


Fig. S4 sep_c – V_g plot of the sample w/o Al_2O_3 (0 cycle of ALD) in 0.2 V steps (error bars, 1σ of the fits, are smaller than the symbols); lower panel, residuals from the linear fit (dashed line; gray band, ± 0.012 eV).