Supplementary Material for Band offsets at amorphous-crystalline Al_2O_3–$SrTiO_3$ oxide interfaces

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Microstructural Analysis of Al_2O_3

X-ray diffraction (XRD) measurements were conducted to rule out potential crystallinity of the Al_2O_3 layer, using a Rigaku Smartlab diffractometer with a 2-bounce Ge (220) monochromator. The diffraction pattern acquired for the thick (10 nm) Al_2O_3 film is presented in Fig. S1, only substrate peaks are observable, verifying the amorphous nature of the layer.

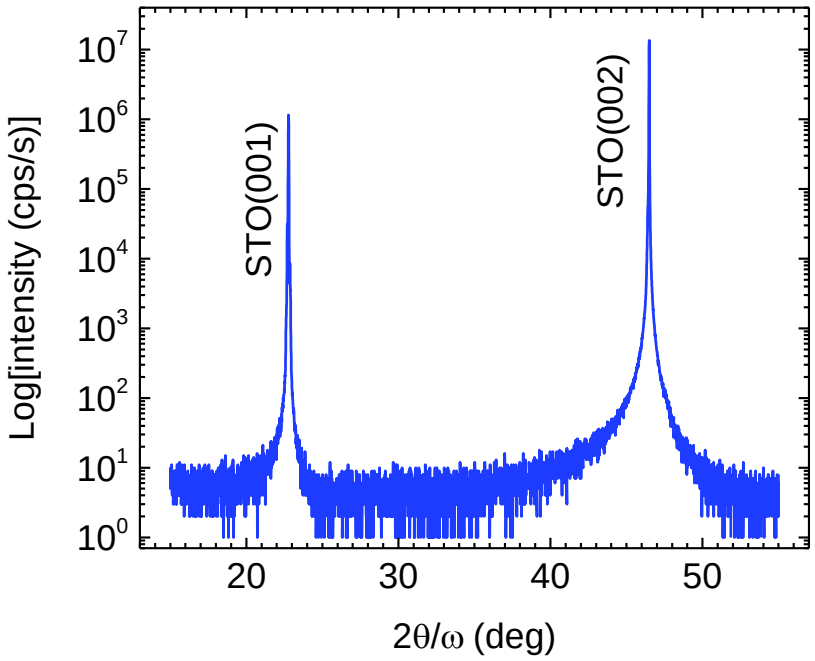

FIG. S1. X-ray diffraction data acquired from the thick Al_2O_3-STO structure.

Discussion of Band Bending and Built-in Potentials

The effect of STO band bending on the overall analysis was found to be negligible. Examining the three different 'bare' substrates, the Ti $2p_{3/2}$ to the VB maximum (VBM) energy difference was determined as: 455.87, 455.93 and 455.99 eV for undoped, 0.05% and 0.5%(wt) Nb-doped samples, respectively. This 0.12 eV difference is smaller than our conservative estimation of a ±0.2 eV uncertainty in the VBM determination. The fact that a metallic [0.5%(wt) Nb-doped] and an insulating (undoped) substrates show such small differences indicates that while band bending may exist, its effect on the interpretation of the data is negligible compared to the experimental uncertainty. Importantly, the full width at half maximum (FWHM) of the Ti $2p_{3/2}$ peak is 0.97, 0.97 and 0.94 eV for undoped, 0.05% and 0.5%(wt) Nb-doped samples, respectively (Table S1). If significant band bending existed, a distinct doping-dependent broadening of this feature was to be expected,[1] further supporting the negligible effect of possible band bending on the interpretation of the data.

Table S1. Summary of the fitting parameters of all the features used in the band offset analysis. BE, FWHM and VBM denote binding energy, full width at half maximum and valence band maximum, respectively. The Al 2p peak was fit with a doublet that includes an additional Al $2p_{1/2}$ component having the same FWHM, 1:2 area ratio and a 0.4 eV higher BE.

Doping %(wt) Nb	**Sample**	**Ti $2p_{3/2}$**		**Al $2p_{3/2}$**		**VBM**
		BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)
0.5%	Thick Al_2O_3	-	-	74.40	1.48	3.7
	Thin Al_2O_3	458.30	0.95	74.40	1.48	-
	Bare	458.30	0.94	-	-	2.31
0.05%	Thin Al_2O_3	458.57	0.96	74.40	1.50	-
	Bare	458.57	0.97	-	-	2.64
undoped	Thin Al_2O_3	458.22	0.97	74.40	1.49	-
	Bare	458.22	0.97	-	-	2.35

This discussion doesn't rule out possible a built-in potential across the Al_2O_3 layer. However, the FWHM of the Al $2p_{3/2}$ peak is identical, within 0.02 eV, for all samples containing Al_2O_3; these include the thick and the thin Al_2O_3 layers, the later both with doped and undoped substrates (Table S1). A built-in potential is expected to be manifested in broadening of these features,[1] and it remains unlikely that a thick layer would present the same internal field as a thin layer, and that an insulating and conductive substrates would result in the same screening and thus built-in potential in amorphous Al_2O_3. However, a rigorous conclusion regarding built-in potentials cannot be based on these observations alone. Unlike the band offset analysis which only relies on relative energy differences, a reliable estimation of the built-in potential would require the use of the absolute values of the binding energies. Reliable absolute values require meticulous and accurate charge compensation and spectrometer calibration.[2,3] Due to the highly insulating nature of Al_2O_3 and the fact that one of the substrates is insulating as well, we did not attempt to estimate the built-in potential owing to the possible errors stemming from charging of the sample. This charging has no effect on the band offset measurements reported in the paper, since no absolute energy values are needed there.

Bibliography

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