Supporting Information

Sputtering Deposition of Transition Metal Oxide on Silicon : Evidencing the role of oxygen bombardment for Fermi level pinning.

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1 Si/SiO$_2$ surface conditioning and hydrogen passivation

As described in the article, sample used for Si/SiO$_2$ interface experiments in the DAISY-MAT system are prepared in a furnace beforehand. Their exposition to air during storage and transportation is then unavoidable. Various contaminant (carbon, hydroxide) might be found on the surface which have to be removed in order to carry out interface experiments on controlled surfaces, especially to eliminate uncertainty on the results and improve experimental repeatability. Looking more into details at the XPS spectra of the Si 2p region, one can notice difference in the Si^0 and Si^{IV} peak position with regards to the cleaning method.

The Si^0 peak position can be of main interest to evaluate the quality of the Si/SiO$_2$ interface. We assumed that the closer the Si^0 peak position to the calculated flat band position, the better it is. Calculated flat-band position, where no charge accumulation (negative or positive) occurs at the silicon surface, has been calculated to be 99.574 eV in taking a Si^0 to the VBM distance of 98.74 eV [1]. Thus, Si 2p spectra for any ex-situ sample shows that the Si^0 peak position is about 0.4 eV to higher binding to the calculated flat-band position (Figure 1). It would mean that contaminants bend the bands downward leading to the accumulation of electrons at the surface of the silicon. This configuration is not an optimal starting condition for interface experiments. Therefore, the contaminants have to be removed but it should not have any detrimental effect on the Si/SiO$_2$ interface quality. This is why, an effective cleaning process, additionally to remove trace of ex-situ contamination has to preserve the sample surface quality and the sample surface integrity.

Figure 1 provides an overview of the ΔSi 2p peak distance (ΔSi 2p =Si^{IV}-Si^0) relatively to the Si^0 peak position. The cleaning of the Si/SiO$_2$ has been evaluated by in-situ XPS in the DAISY-MAT system. Three methods have been employed: thermal cleaning in oxygen, cleaning by exposure to an oxygen plasma source and with an hydrogen plasma source. Thermal cleaning did not provide satisfying results as the Si^0 peak position is unchanged after the process. Oxygen plasma cleaning increased the S^0 peak position too far to the right of the calculated flat-band position. Hydrogen cleaning followed by an hydrogen passivation step of the Si/SiO$_2$ samples (see Article) provide little data dispersion in comparison to the others methods. In addition relatively closed Si^0 peak position to the calculated flat-band position could be obtained. As the passivation of the Si/SiO$_2$ surface by atomic hydrogen generated from a plasma source has been already reported in the literature, it has

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been decided that cleaning and passivation of the samples will be subsequently realized by exposing them to a hydrogen plasma source (details in the article).

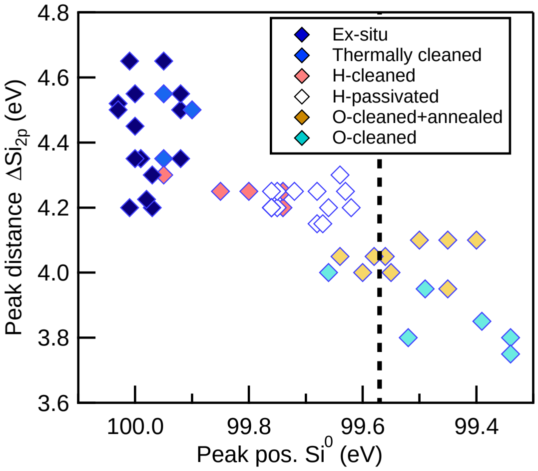

Figure 1: Right plot: Compilation of Si^0 peak position vs ΔSi 2p=Si^0(3/2)-Si^{IV} peak distance for different Si/SiO_2 surface preparation. The vertical dotted line represents the calculated flat-band position of the Si^0 main peak. *Thermal cleaning* is realized at 200 ˚C for 2 h in 1 Pa O_2, *O-cleaned* corresponds to exposing the Si/SiO_2 surface to an oxygen plasma source for 10 mins at RT which can be subsequently followed by thermal heating in vacuum at 200 ˚C to remove peroxy species (*O-cleaned+annealed*). *H-cleaned* stands for exposing the sample to the hydrogen plasma source and *H-passivated* to hydrogen surface passivation as detailed in the article.

2 Reactive sputtering on a thick SiO_2 layer

A similar electronic feature in the Si 2p region as reported in the article, and associated to defective electronic state, has been observed for sputtered Barium Strontium Titanate (BST-BaO_4SrTi) onto Si(100)/SiO_2/TiO_2/Pt(111) where the signal of elemental Si^0 is not detected (no signal from the Si/SiO_2 interface). The silicon dioxide layer is thicker than in the article and is about 5 nm. The BST was RF-sputtered in Ar:O_2 atmosphere (ratio 99:1) at 650 ˚C as detailed by Schafranek *et al.* [2]. Although the photo-emitted electron are from bulk SiO_2, the in-situ XPS spectra (Figure 2) evidence, during interface experiments, the built-up of an additional electronic state in the Si 2p region as for reactive DC sputtering of NiO (labelled $Si^{Def.}$ on Figure 2). Therefore, similarly, the experimental results might suggest the oxygen from the BST target or from the sputtering atmosphere are ionized and accelerated towards the sample, which would diffuse through the TiO_2/Pt layers, until it reaches the SiO_2 layer where the ionized oxygen atoms are implanted. The experiment suggests that the defective electronic state is formed in the bulk of the SiO_2 layer.

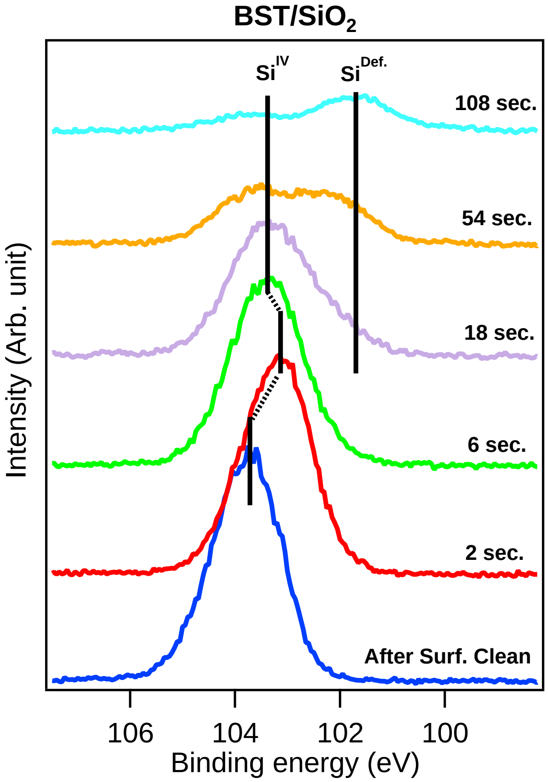

Figure 2: Si 2p region measured by in-situ XPS during BST interfacing on a thick SiO$_2$ layer. The sputtering of BST onto SiO$_2$ results onto similar electronic feature as observed in the article. Data were obtained in the work of Schafranek *et al.* [2].

References

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[2] R. Schafranek, A. Giere, A. G. Balogh, T. Enz, Y. Zheng, P. Scheele, R. Jakoby, and A. Klein, “Influence of sputter deposition parameters on the properties of tunable barium strontium titanate thin films for microwave applications,” *Journal of the European Ceramic Society*, vol. 29, no. 8, pp. 1433–1442, 2009.