

Supplementary Information

In situ study of the electronic structure of atomic layer deposited oxide ultrathin films upon oxygen adsorption using ambient pressure XPS

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(1) Work function measurement

For work function measurement, Ar 2p and C 1s spectra were recorded by APXPS in Ar atmosphere with the HOPG was applied with different bias (-2 to +2 V). An calibration curve was established for the relationship of work function and Ar core level binding energies.¹ The clean HOPG surface was prepared by cleave using Kapton tape. The HOPG sample was mounted with insulating ceramic, makes the HOPG sample is isolated from the XPS system. An external power supply was connected to the HOPG sample.

At first, we compared the binding energy of C 1s with the external bias. Fig. S1(a) is the spectra of C 1s with different applied biases. As shown in Fig. S1(a), the peak of C 1s shifts with the applied biases. Try to more clearly show their relationship, we plotted the relationship between applied biases with the binding energies of C 1s. As shown in Fig. S1(b), the binding energy of C 1s shifts linearly with the applied biases. The values of shift are exact same with

the applied biased. This gives us the idea that all the energy levels in HOPG should shift same with the potential we added.

The applied bias on HOPG were +2, +1, 0, -1 and -2 V, subsequently lead to change same change of the vacuum level. If references to the Fermi level of analyzer, this is equivalently using samples with the work function of 2.6 eV, 3.6 eV, 4.6 eV, 5.6 eV and 6.6 eV, respectively. The core level XPS of Ar 2p were measured at the meanwhile. As shown in Fig. S2(a), the spectra of Ar 2p shift vs. the applied bias. This demonstrates that the binding energy of Ar has been influenced by the vacuum level of the samples. Then we plotted out the binding energy of Ar 2p_{3/2} and the work function relationship, and fitting it to get the equation of work function and Ar 2p_{3/2} binding energy:

$$\Phi_{\text{samp}} = -1.03 \text{ BE}_{\text{gas}} + 256.235$$

Where Φ_{samp} is the work function, BE_{gas} is the binding energy of Ar 2p_{3/2}.

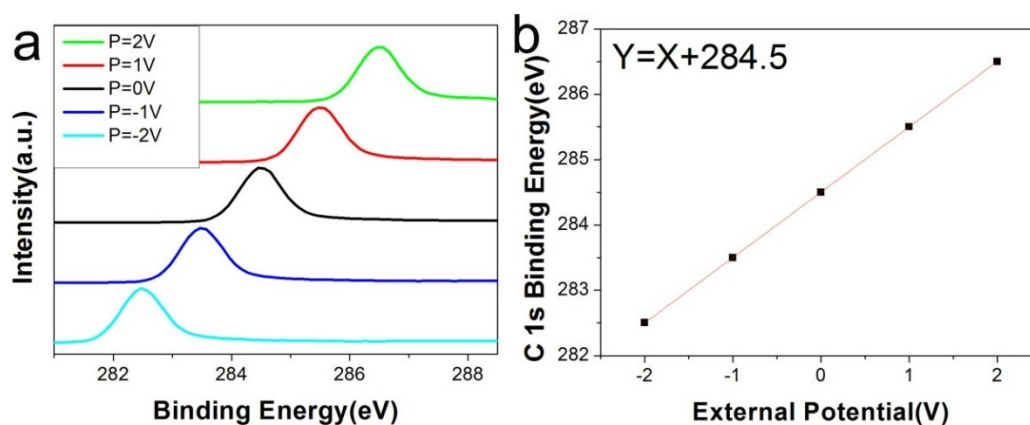


Fig. S1 (a) C 1s spectra of HOPG with different applied bias. (b) Linear fitting of binding energy of C 1s versus the applied bias.

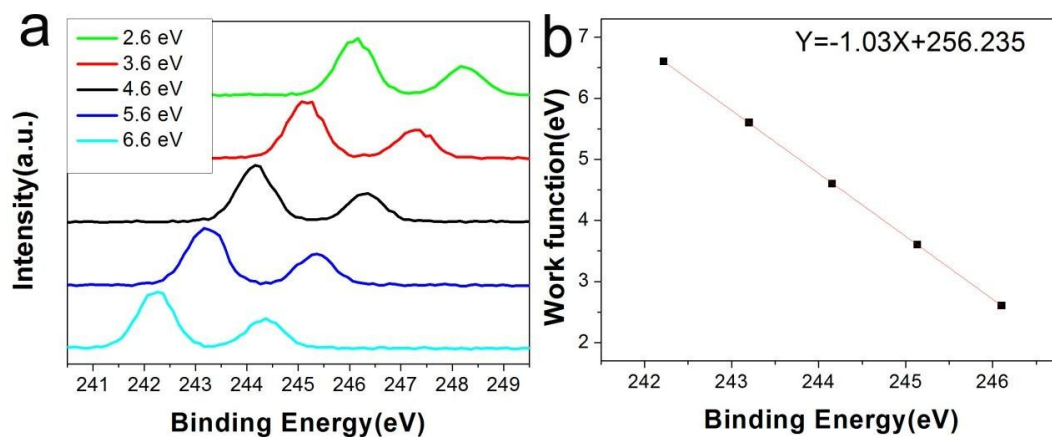


Fig. S2 (a) Ar 2p spectra of gas phase Ar with the work function changes, (b) relationship of work function with binding energy of Ar 2p_{3/2}.

(2) Band bending of Si substrate

The core level binding energy change of Si substrate after oxygen exposure is less than the change of these oxide ultrathin films, as shown in Fig. S3 and Fig. S4. There exists a layer of naturally oxidized SiO₂ between the Si substrate and the ultrathin film. As observed in the Si 2p XPS spectra, peaks at ~99 eV were attributed to Si 2p from Si substrate and peaks at 104 eV were attributed to Si 2p from SiO₂. And the Al 2p binding energy change of Al₂O₃ ultrathin film sample is ~0.61 eV after oxygen exposure, and that of Si 2p from the Si substrate and SiO₂ is 0.31 and 0.52 eV, respectively. Only oxygen adsorbed on top of ultrathin film surface will lead to this results, otherwise the binding energy change of Al 2p will be less than that of Si 2p. Similar phenomenon were also observed on the ZnO and TiO₂ samples.

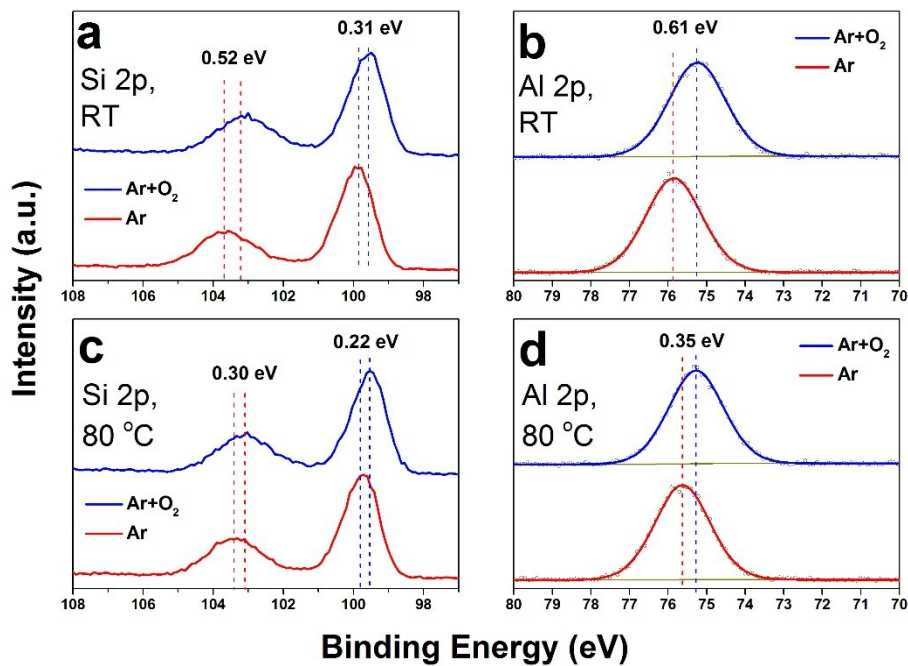


Fig. S3 XPS spectra of Si 2p of the Si substrate and Al 2p of the Al₂O₃ ultrathin film under Ar (red curves) and Ar+O₂ atmospheres (blue curves): (a) Si 2p of Si substrate at room temperature, (b) Al 2p of Al₂O₃ at room temperature, (c) Si 2p of Si substrate at 80 °C and (d) Al 2p of Al₂O₃ at 80 °C.

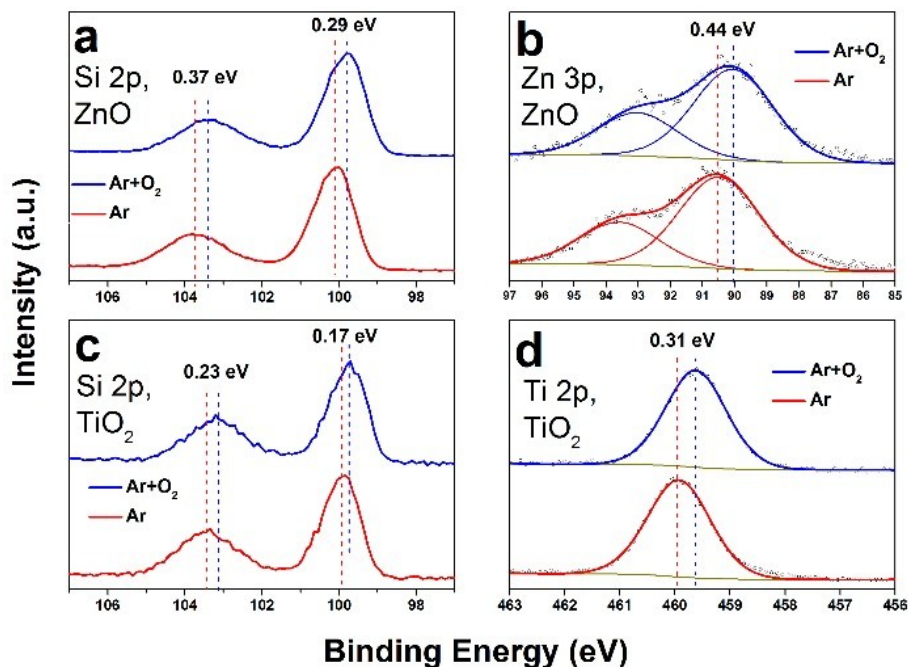


Fig. S4 XPS spectra of the Si substrate and the ZnO and TiO₂ ultrathin films under Ar (red curves) and Ar+O₂ atmospheres (blue curves) at room temperature: (a) Si 2p and (b) Zn 3p of ZnO sample, (c) Si 2p and (d) Ti 2p of TiO₂ sample.

(3) Coverage calculation:

We use the equation (Eq.1) for surface space charge on semiconductor to calculate the coverage of strongly chemisorbed oxygen,

$$Q_s = (2 \epsilon_{rs} \epsilon_0 q N_d V_s)^{1/2} \quad (1)$$

where Q_s is the surface charge density, ϵ_{rs} is the relative dielectric constant, ϵ_0 is the vacuum dielectric constant, q is elementary charge, N_d is the carrier density, and V_s is the potential of band bending.

To illustrate the coverage level of the strongly chemisorbed oxygen, we take the Si as the example in here. For doped Si, if the doped density is 10^{16} cm^{-3} and band bending is 0.5 V, the calculated coverage is $\sim 2.5 \times 10^{-4}$ monolayer. These results are consistent with previous reports that the coverage of strongly chemisorbed oxygen is less than $\sim 10^{-3}$ monolayer due to the Weisz limitation.^{2,3}

For the weak chemisorbed oxygen, we calculated the coverage by the electron affinity changes using “parallel plate capacitor” model.⁴ The estimated coverage of weak chemisorbed oxygen is about $\sim 10^{-2}$ monolayer for Al_2O_3 and ZnO at room temperature.

(4) O 1s XPS spectra

Fig. S5 (a) shows the O1s spectra in Ar (red line) and in Ar/O₂ mixture (blue line) on the Al_2O_3 sample, respectively. The oxygen adsorption mainly induces a red shift of the interfacial O1s peak by $\sim 0.6 \text{ eV}$. The comparison of the peak shapes between the two O1s spectra in Fig. S5(b) shows that there is not noticeable change induced by the oxygen adsorption. The negligible adsorption-induced change indicates that the O1s spectra are dominated by the signal from oxides on the sample and the adsorbed oxygen species are not resolvable from the O1s spectra. According to our estimation shown in supporting information, there are only $\sim 10^{-4}$ monolayer of strongly chemisorbed oxygen species and 0.01 monolayer of weakly chemisorbed oxygen species. Such a low coverage of the adsorbed oxygen is below the XPS detection limitation.

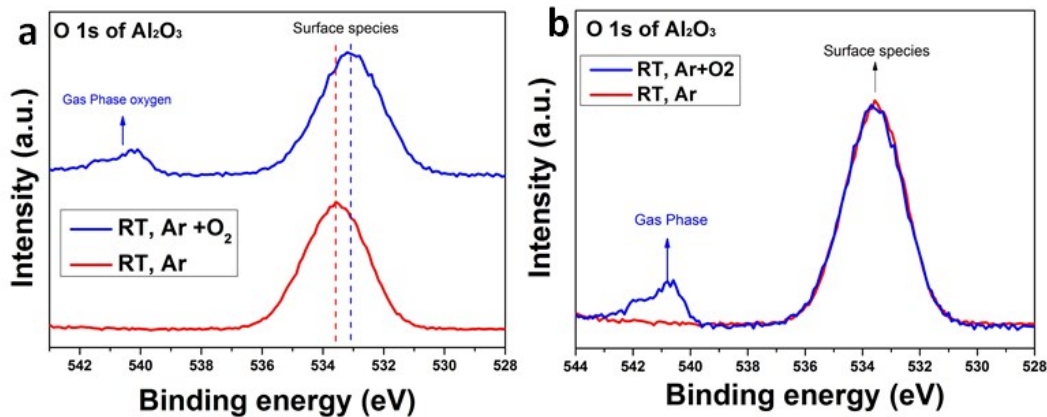


Fig. S5 (a) The O1s spectra of Al₂O₃ sample at room temperature in Ar (red line) and Ar/O₂ (blue line) mixtures, respectively. (b) The comparison of the peak shapes of the two spectra in (a). In order to comparing, the two spectra are normalized by their peak areas of surface species, respectively, and then the spectrum in Ar/O₂ mixture is shifted by ~ 0.6 eV to the high bonding energy.

References

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