

Supplemental Information

Near Ambient Pressure X-ray Photoelectron Spectroscopy Study of the Atomic Layer Deposition of TiO₂ on RuO₂(110)

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RuO₂ substrate

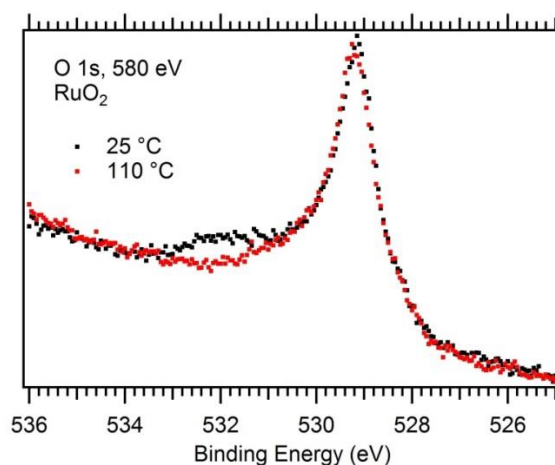


Figure S1. O 1s spectra of the RuO₂(110) substrate at 25 °C (black dots) and 110 °C (red dots). No background is subtracted from the spectra.

The O 1s spectrum of the RuO₂ substrate in Figure S1 shows that there is water on the surface at room temperature, indicated by the peak around 532 eV. Hydroxyl groups also contribute to the intensity of the high binding energy shoulder around 530 eV.¹ The water is removed at 110 °C, the temperature used for the ALD studies.

Peak Fitting

The Ti 2p spectrum of the third water half-cycle was fit to determine if there was a TiN component, which would occur at least 3 eV lower than the TiO₂ component. Only the Ti 3p_{3/2} peak was fit due to the complexity of the spectrum at high binding energies where there is intensity from satellites and the Ru 3p_{3/2} from the substrate around 461.5 eV overlapping with the Ti 2p_{1/2} component. The two peaks in Fig. S2 are 1.4 eV and 2.8 eV lower than the main component. The component at 2.8 eV lower than the main peak is nearly consistent with that of TiN and cannot be excluded. However, there is not a significant amount. The component 1.4 eV lower than the main line is assigned to Ti³⁺ coordinated to imide ligands.

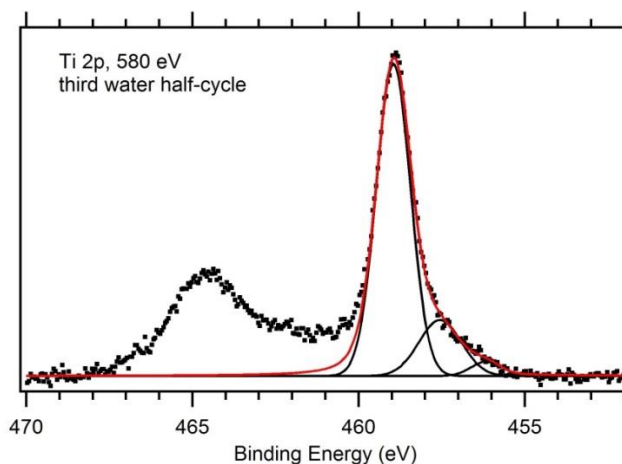


Figure S2. Ti 2p spectrum (black dots) of the third water half-cycle. The red line is the fit of three components (black lines). The spectrum has a polynomial background removed and is fit with Voigt functions.

The N 1s spectra collected at each half-cycle for 3 full ALD cycles in a second iteration of the experiment are shown in Fig. S3. The areas of the components in the fits were used to generate the graph in Figure 5 of the main manuscript.

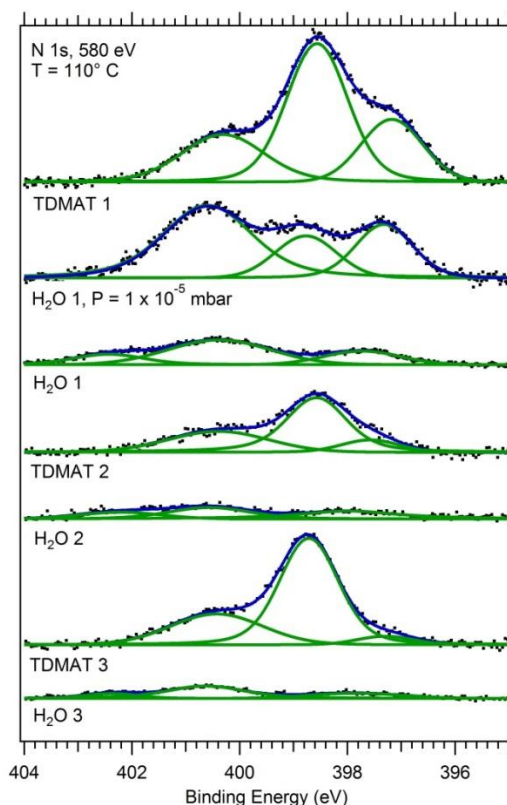


Figure S3. N 1s PE spectra (black dots) and fits (blue lines) of the Voigt functions (green lines) representing the different chemical species: imine at 397.2 eV, amido ligand at 398.6 eV, amine at 400.3 eV, and alkylammonium cation at 402.4 eV. The TDMAT pressure of the first half-cycle was 0.1 mbar and 0.01 mbar for the second and third half-cycles. The first two H₂O cycles are at 1 mbar and the third is at 0.01 mbar.

The O 1s spectra at each half-cycle for 3 full ALD cycles are shown in Figure S4. The binding energies of the components resulting from each fit are listed in Table 1 in the main manuscript. Since this experiment was the second iteration, there was a background pressure of TDMAT in the analysis chamber. Upon introduction of the sample into the analysis chamber, TDMAT begins to adsorb. Additionally, molecular water is known to adhere to RuO₂ at room temperature and likely aids the chemisorption onto the clean RuO₂ surface. For these reasons, the initial RuO₂ O 1s spectrum is different from that presented in Fig 6a of the main manuscript.

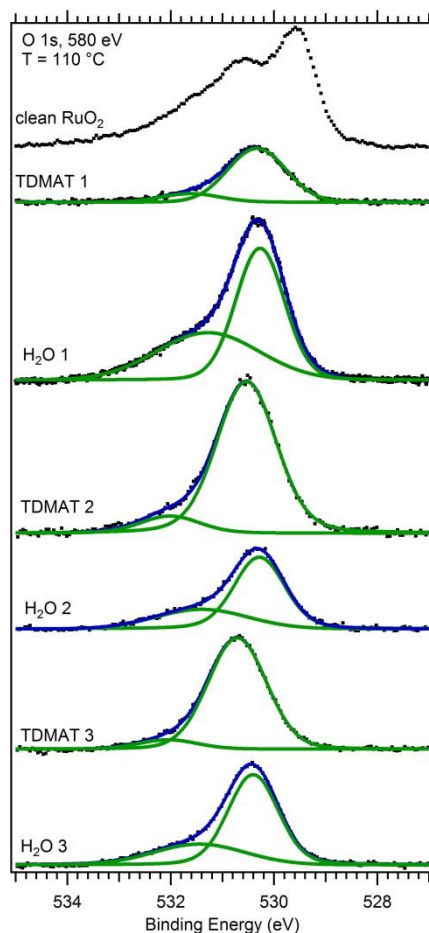


Figure S4. The O 1s PE spectra during the half-cycles listed. The clean RuO₂ was exposed to a background pressure of TDMAT. The first TDMAT half-cycle was collected under a pressure of 0.1 mbar and the second and third under 0.01 mbar. The first and second H₂O half-cycles were under a pressure of 0.1 mbar and the third was 0.01 mbar. All spectra except the first one were collected with the sample temperature at 110 °C. The RuO₂ spectrum was collected at 30 °C.

Room temperature adsorption and heating of TDMAT on RuO₂

The adsorption of TDMAT on RuO₂ at room temperature is followed in the Ru 3d (Fig. S5), O 1s (Fig. S6), and N 1s (Fig. S7) spectra. The large shoulders at higher binding energy of the O 1s spectrum are hydroxyl groups and molecular water, known to be present at room temperature on RuO₂.¹ A pressure of 0.1 mbar is needed to form a multilayer of TDMAT on the surface as indicated by the disappearance of the Ru 3d and O 1s PE peaks after about 9 minutes at this pressure. Additionally, the amido ligand binding energy is higher at room temperature and a pressure of 0.1 mbar compared to lower coverages at higher temperature, as discussed in the main article. The binding energy appears to have stabilized around 110 °C (Fig. S7), indicating that the multilayer is desorbed. In the Ru 3d spectra at 110 °C, the low binding energy surface peak has grown larger and become an interface peak.

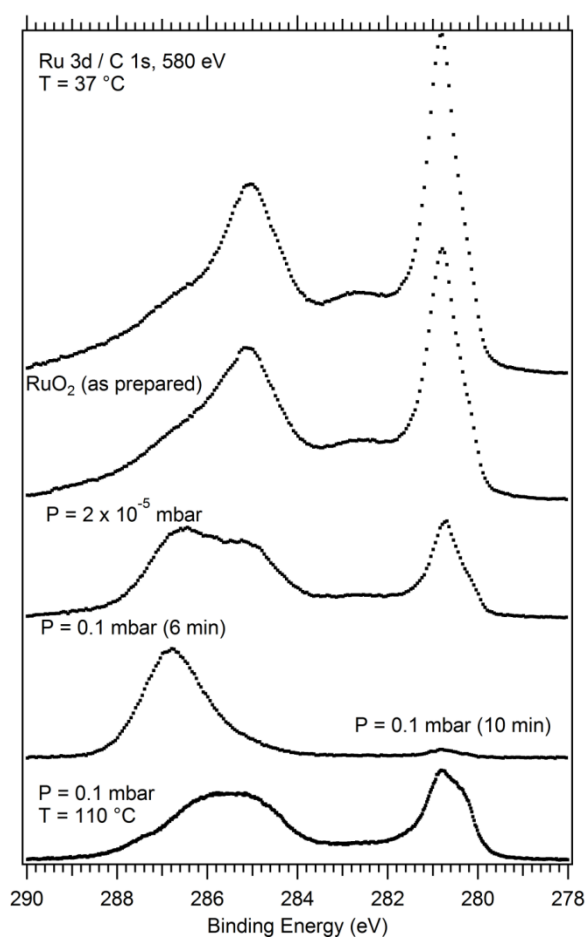


Figure S5. Ru 3d and C 1s PE spectra of TDMAT dosed at room temperature on RuO₂ and then heated to 110 °C.

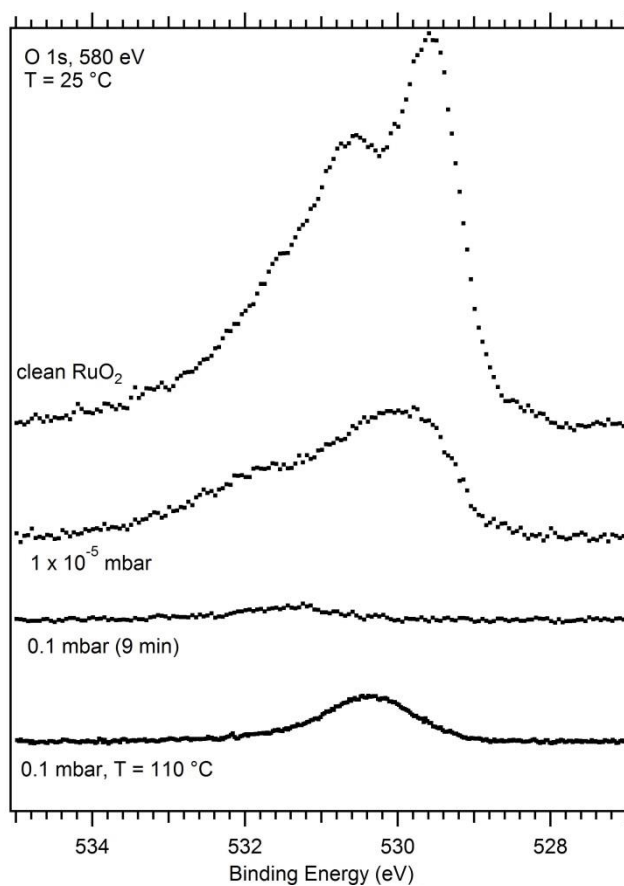


Figure S6. O 1s XP spectra of TDMAT dosed on RuO₂ beginning at room temperature at the pressures listed. A multilayer is present after 9 minutes at a pressure of 0.1 mbar. The final spectrum was collected at 110 °C.

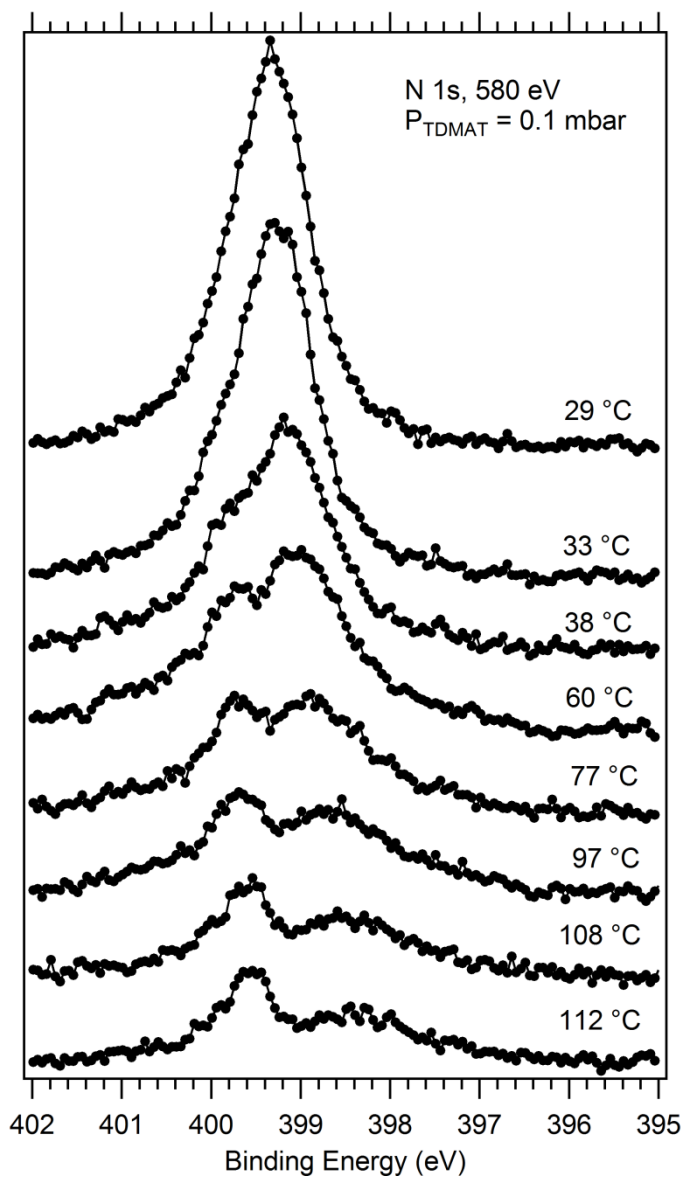


Figure S7. N 1s spectra on RuO₂ at room temperature and while heating under a TDMAT pressure of 0.1 mbar.

¹ Foelske, A; Barbieri, O.; Hahn, M.; Kötzt, R. An X-ray Photoelectron Spectroscopy Study of Hydrated Ruthenium Oxide Powders with Various Water Contents for Supercapacitors. *Electrochim. Solid-State Lett.* **2006**, 9, A268-A272.