Supporting information

The effect of ruthenium oxidation on the decomposition of SiH_4

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1. XPS peak fitting procedure – this section provides the details of the fitting procedure employed to obtain the results presented in the manuscript.

For the Ru 3d region, a Shirley background was used. The energy difference and area ratio (Ru $3d_{5/2}$:Ru $3d_{3/2}$=1.5) of the spin-orbit-split components of Ru 3d was constrained for all fits. The fitting parameters were optimized using a reference spectrum acquired from clean Ru(0001). Upon partial and near-complete oxidation of the surface, additional Ru oxide components were introduced while maintaining the same relative constraints between the 5/2 and 3/2 components. For the metallic and oxide Ru 3d components, Doniach–Šunjić–Gaussian (DS-G) line shapes were used to account for the metallic character of Ru and RuO_2. An increased Lorentzian width was allowed for the Ru $3d_{3/2}$ component to account for Coster–Kronig broadening. The thin oxide components and satellite features in the Ru 3d region were fitted using Voigt line shapes. The corresponding satellite peak areas were constrained to also maintain a 1.5 area ratio between the Ru $3d_{5/2}$ and Ru $3d_{3/2}$ components. The area ratio of the satellite peak and the main core level peak was determined from calibration measurements on reference oxide spectra and subsequently kept constant for all oxidized Ru components throughout the fitting procedure. For the pristine Ru and the thick oxide, the fit in Table I was used. For pristine Ru, the area of the oxide-related components decreased to zero, reflecting the absence of oxide species. The electronically different thin oxide required different fit parameters, characterized by a small shift of the oxidized Ru core level and the absence of the characteristic satellite of rutile RuO_2. The fit parameters are provided in Table II. The mixed oxide was fitted accounting for the coexistence of thin oxide and thicker (RuO_2) oxide components.
For both, O 1s and Si 2p spectra, the focus was the determination of the total area of peaks emerging at a priori unknown binding energies and peak shapes. No constraints were applied to those peaks other than the energy difference and peak area ratio of the spin-orbit split for the Si 2p components. For all Si 2p spectra, a Shirley background was used. The individual Si components were fitted using Voigt doublets, reflecting the spin-orbit split components of Si $2p_{3/2}$ and Si $2p_{1/2}$ with a fixed area ratio of 2:1 and a binding energy difference of 0.6 eV between the two components. The reported binding energies (BEs) are given by the peak position resulting from summing up the components of the fitted double Voigt. The O1s spectra were fitted using Voigt peak shapes.

Pristine Ru & Thick RuO_2	Ru $3d_{5/2}$	Ru $3d_{3/2}$	RuO_2 $3d_{5/2}$	RuO_2 $3d_{3/2}$	RuO_2 $3d_{5/2}$ satellite	RuO_2 $3d_{3/2}$ satellite
Peak shape	DS-G	DS-G	DS-G	DS-G	Voigt	Voigt
BE (eV)	280.1	284.3 (BE Ru $3d_{5/2}$+4.2)	280.7 (BE Ru $3d_{5/2}$+0.6)	284.9 (BE RuO_2 $3d_{5/2}$+4.2)	282.5 (BE Ru $3d_{5/2}$+2.4)	286.7 (BE RuO_2 $3d_{5/2}$ satellite + 4.2)
Lorentzian width (eV)	0.190	0.600	0.200	0.700	0.200	0.700
Lorentzian asymmetry (eV)	0.045	0.035	0.130	0.114	-	-
Gaussian width (eV)	0.400	0.478	0.467	0.467	2.000	2.000

Table SI: XPS fitting parameters for pristine Ru and RuO_2. BE refers to the fitted binding energy of the peak component.

Thin oxide	Ru $3d_{5/2}$	Ru $3d_{3/2}$	RuO_2 $3d_{5/2}$	RuO_2 $3d_{3/2}$	RuO_2 $3d_{5/2}$ satellite	RuO_2 $3d_{3/2}$ satellite
Peak shape	DS-G	DS-G	Voigt	Voigt	Not present	Not present
BE (eV)	280.1	284.3 (BE Ru $3d_{5/2}$+4.2)	281.0 (BE Ru $3d_{5/2}$+0.9)	285.2 (BE RuO_2 $3d_{5/2}$+4.2)	-	-
Lorentzian width (eV)	0.190	0.600	0.001	0.238	-	-
Lorentzian asymmetry (eV)	0.045	0.035	-	-	-	-
Gaussian width (eV)	0.400	0.478	0.740	0.848	-	-

Table SII: XPS fitting parameters for thin RuO_2. BE refers to the fitted binding energy of the peak.

Panel Fig. 3	Si Peak	BE apparent max. (eV)	BE Si $2p_{3/2}$ (eV)	Lorentzian width (eV)	Gaussian width (eV)	Type
(a) - Pristine	Si	99.6	99.6	1.51	0	2×Voigt
(b) - Thin oxide	Si-1	103.2	103	0.32	1.20	2×Voigt
(b) - Thin oxide	Si-2	100.4	100.2	0	1.49	2×Voigt
(c) - Mixed oxide	Si-1	103.2	103	0.32	1.20	2×Voigt
(c) - Mixed oxide	Si-2	101.8	101.7	0	1.49	2×Voigt
(c) - Mixed oxide	Si-3	100.4	100.2	0	1.49	2×Voigt

Table SIII: XPS fitting parameters for Si used in Figure 3 of the manuscript. "BE apparent max." refers to the binding energy of maximum intensity for the sum of the Si $2p_{3/2}$ and Si $2p_{1/2}$ peaks spaced 0.6 eV, while BE Si $2p_{3/2}$ is the binding energy of the first component only.

Panel Fig. 3	O Peak	BE (eV)	Lorentzian width (eV)	Gaussian width (eV)	Type
(a) - Pristine	O	531.3	0	1.38	Voigt
(b) - Thin oxide	O-1	532.2	0	2.36	Voigt
(c) - Mixed oxide	O-1	529.3	0	0.72	Voigt
(c) - Mixed oxide	O-2	529.9	0	1.34	Voigt
(c) - Mixed oxide	O-3	531.8	0	2.59	Voigt

Table SIV: XPS fitting parameters for O used in Figure 3 of the manuscript.

2. LEED patterns - To verify the crystallographic orientation and surface order of the sample, low-energy electron diffraction (LEED) measurements were performed following the standard cleaning procedure described in the manuscript. The resulting diffraction pattern exhibits the expected hexagonal symmetry of a well-ordered Ru(0001) surface, confirming the surface orientation and long-range order.

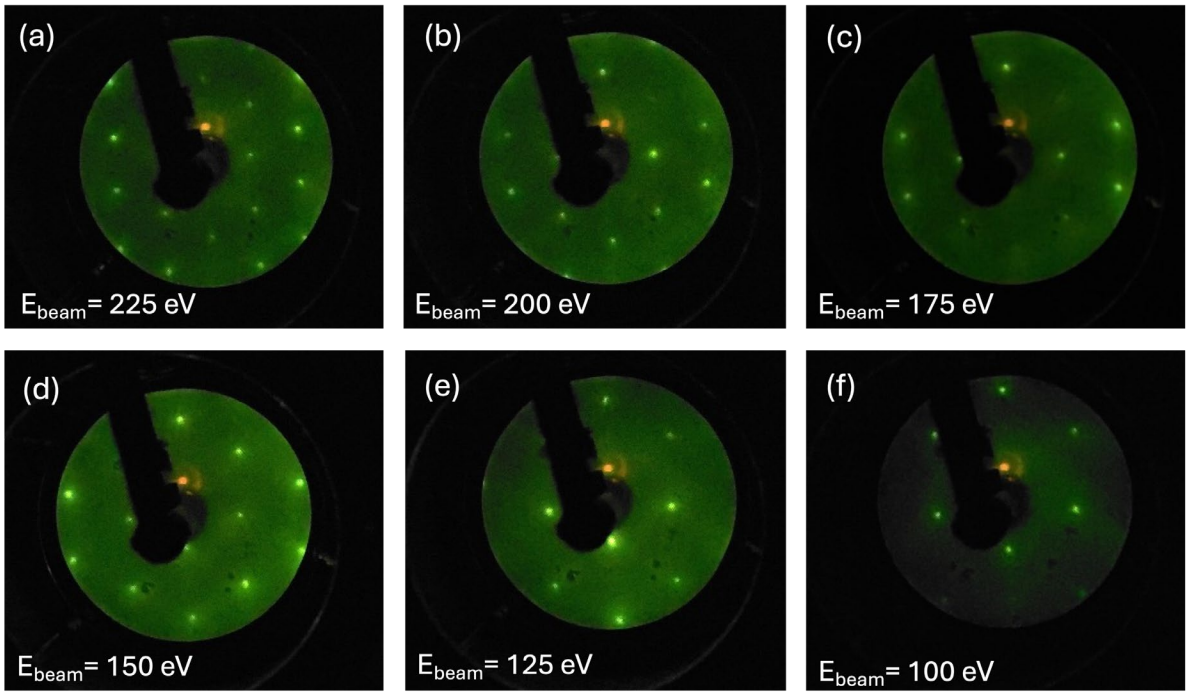

Figure S1: LEED patterns of Ru(0001) for varying beam energy.