Growth of Alumina Overlayer Deposited on Au_{101}/TiO_2 Catalyst Model Via Atomic Layer Deposition

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Table S1: List of samples investigated through this project.

Samples	Composition	Characterisation
Free of Au_{101} Samples		
0 ALD	TiO_2	XPS, and ARXPS
1 ALD	AlO_x/TiO_2	XPS, and ARXPS
5 ALD	AlO_x/TiO_2	XPS, and ARXPS
10 ALD	AlO_x/TiO_2	XPS, and ARXPS
Samples with Au_{101} clusters		
0 ALD	Au_{101}/TiO_2	XPS, ISS, and NICISS
1 ALD	$AlO_x/Au_{101}/TiO_2$	XPS
2 ALD	$AlO_x/Au_{101}/TiO_2$	NICISS
5 ALD	$AlO_x/Au_{101}/TiO_2$	XPS, ISS, and NICISS
10 ALD	$AlO_x/Au_{101}/TiO_2$	XPS
Investigation samples		
Calibration Sample	Au/TiO_2	XPS
Al foil sample	Al foil	XPS
O identification sample	Au/SiO_2	XPS

ARXPS Section

The ARXPS concentration depth profile are determined by fitting the measured intensity ratios of each elemental species with calculated intensity ratios through an ARXPS model. In the model the sample is divided into layers with homogeneous thickness and the intensity of electrons emitted of each elemental species forming a given layer is calculated using:

$$I(i,j,\theta) = \frac{d\sigma_i}{d\Omega} n_i(j)\lambda_j(\theta)\left[1 - exp\left(-\frac{d_j}{\lambda_j(\theta)}\right)\right]\prod_{m=1}^{j-1} exp\left(-\frac{d_m}{\lambda_m(\theta)}\right) \quad eq.\ 1$$

where:

$\boldsymbol{n_i}$ is the number density of elemental species i, and z the depth.

$\boldsymbol{E}$ the kinetic energy.

$\boldsymbol{d\sigma/d\Omega}$ the differential photoionization cross-section of the core level of the respective element.

$\boldsymbol{\lambda}$ the electron attenuation length (EAL).

From eq. 1 the relative intensity of each elemental species is calculated. The fitting procedure is based on the following principles:

1. The sample is modelled as a series of finite layers, each with a homogeneous composition and homogeneous thickness. The effective attenuation length (EAL) of electrons varies depending on the composition of each layer.
2. The thickness and composition of each layer are the fitting parameters.
3. The inelastic mean free path (IMFP) of electrons is dependent on their kinetic energy and are taken from[1].
4. The photoionization cross sections of the elements are taken from[2].
5. The thickness of the TiO_2 substrate is assumed to be infinite.
6. Atomic densities (atoms/Å^3) are used to represent the relative depth profile of each element within a layer.

From the concentration depth profiles, the thickness of the ALD layers can be estimated. The layer composition is expressed in terms of atomic densities (atoms/Å^3) as illustrated in[3].

Table S2: Elemental composition of each species of the samples of 1 ALD, 5 ALD, and 10 ALD for 0º, 30º, 45º, 55º, and 60º angles of observations.

ALD Cycles	Emission Angles (θ)	C 1	C 2	C 3	O 1	O 2	Ti	Al
1 ALD	**0^0**	14.2	1.5	0.5	56.5	3.8	20.9	2.5
	30^0	15.3	2.4	0.8	55.0	4.1	20.0	2.5
	45^0	19.1	2.9	0.8	52.4	4.4	17.8	2.5
	55^0	22.2	3.1	0.6	50.4	4.6	16.7	2.4
	60^0	22.0	3.8	1.0	49.3	5.8	16.2	2.7
5 ALD	**0^0**	16.1	1.7	0.6	54.0	4.6	19.8	3.3
	30^0	17.9	1.8	0.5	52.3	4.6	18.7	4.2
	45^0	19.4	2.3	0.6	50.8	5.0	18.1	3.8
	55^0	21.9	3.1	1.1	48.8	4.8	16.2	4.1
	60^0	23.9	3.5	1.0	47.3	4.9	15.3	4.1
10 ALD	**0^0**	18.0	2.5	0.7	49.3	7.6	15.6	6.4
	30^0	20.4	3.1	1.1	47.5	7.7	13.9	6.2
	45^0	23.0	4.6	1.4	44.5	7.9	12.2	6.5
	55^0	25.2	5.4	1.6	42.0	7.8	11.0	6.9
	60^0	25.8	5.57	1.3	42.2	8.2	10.2	6.7

Table S3: XPS calibrated peaks positions(eV) of 1 ALD, 5 ALD, and 10 ALD samples for 0º, 30º, 45º, 55º, and 60º angles of observations.

ALD Cycles	Emission Angle (θ)	C 1 Position (eV)	C 2 Position (eV)	C 3 Position (eV)	O 1 Position (eV)	O 2 Position (eV)	Ti Position (eV)	Al Position (eV)
1 ALD	0^0	284.4	286.0	287.7	530.5	532.0	459.2	74.5
	30^0	284.4	285.7	287.4	530.5	532.0	459.2	74.5
	45^0	284.4	286.0	287.7	530.5	532.1	459.2	74.4
	55^0	284.4	286.1	288.1	530.5	532.1	459.2	74.4
	60^0	284.4	285.8	287.3	530.5	532.2	459.2	74.4
5 ALD	0^0	284.3	285.7	287.4	530.5	531.9	459.2	74.6
	30^0	284.3	285.9	287.9	530.5	531.9	459.2	74.6
	45^0	284.4	285.8	287.5	530.5	532.0	459.2	74.6
	55^0	284.4	285.7	287.1	530.5	532.1	459.2	74.6
	60^0	284.4	285.9	287.9	530.5	532.1	459.2	74.6
10 ALD	0^0	284.3	285.7	287.3	530.5	532.0	459.2	74.6
	30^0	284.3	285.9	287.5	530.5	532.0	459.2	74.6
	45^0	284.3	285.7	287.4	530.5	532.1	459.2	74.6
	55^0	284.4	285.8	287.5	530.6	532.2	459.2	74.6
	60^0	284.4	285.7	287.4	530.6	532.3	459.2	74.6

A single ALD Cycle results (ARXPS)

The XP spectra of C *1s*, O *1s*, Ti *2p*, and Al *2p* for the sample of 1 ALD cycle deposited on plane TiO2 surface. The spectra show in Figure S1, and S2 for 0º of observation and 60º, respectively.

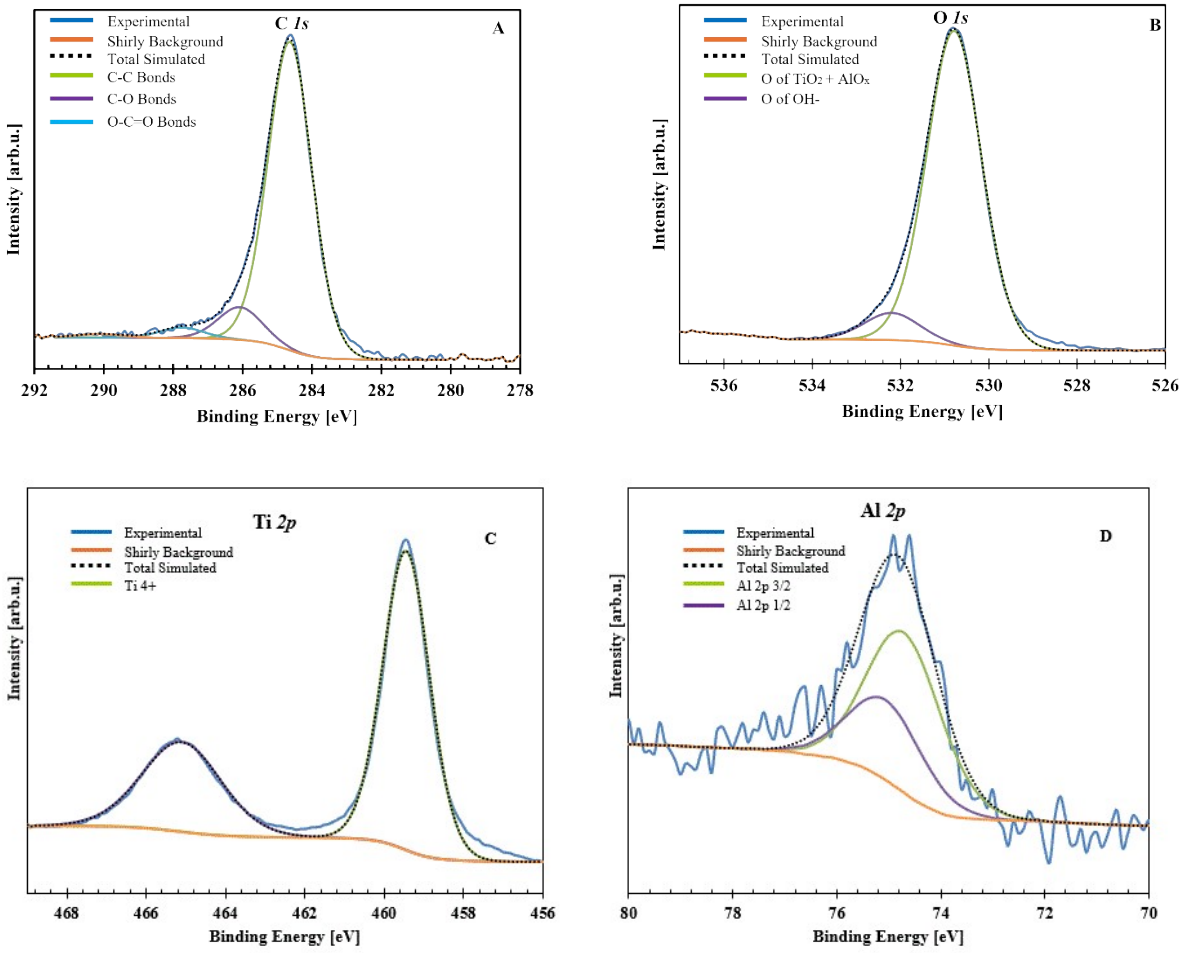

Figure S1: High-resolution XP spectra of 1 ALD-AlO_x deposited onto RF-sputtered TiO_2, fitted with a Shirley background, representing the respective elements of (A) C 1s, (B) O 1s, (C) Ti 2p, (D) Al 2p measured at a 0° emission angle.

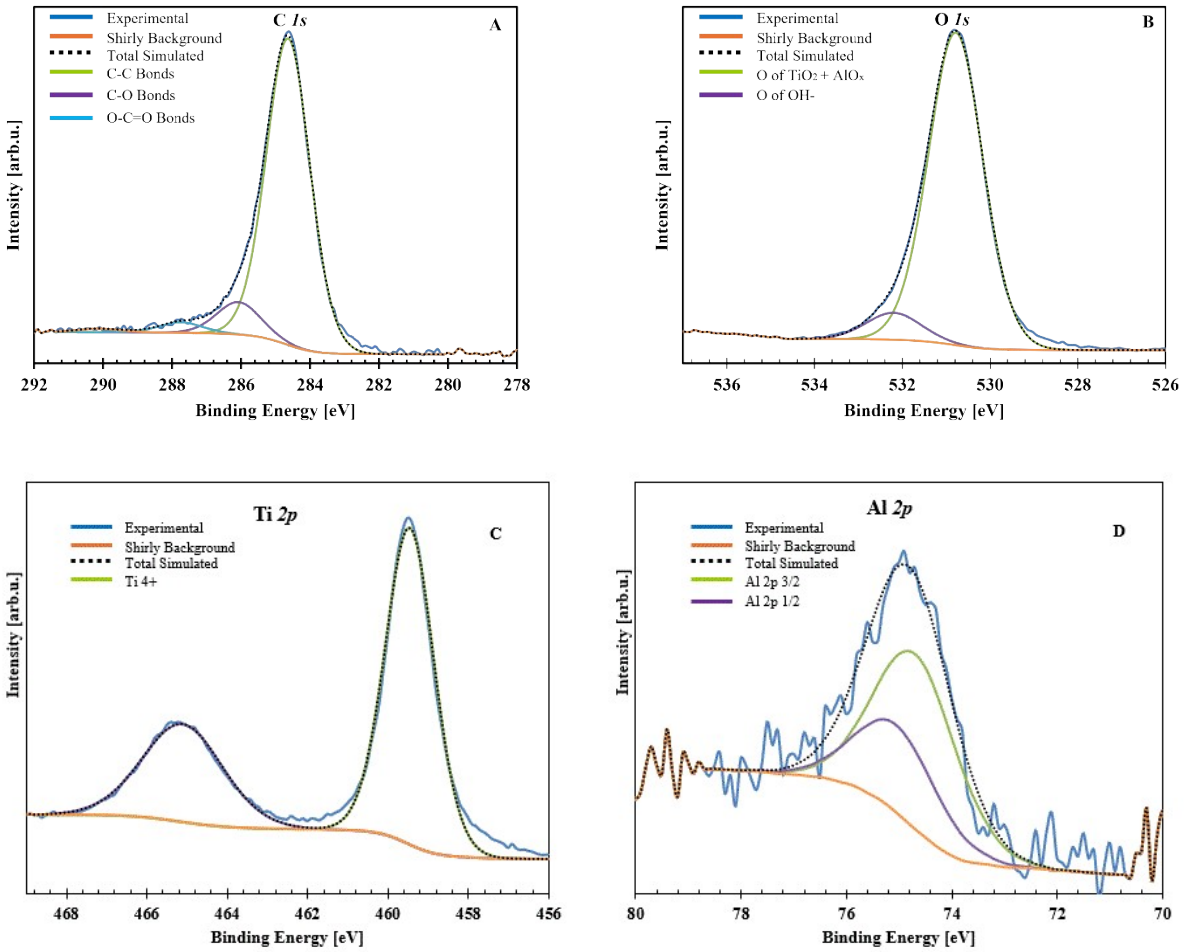

Figure S2: High-resolution XP spectra of 1 ALD-AlO_x deposited onto RF-sputtered TiO_2, fitted with a Shirley background, representing the respective elements of (A) C 1s, (B) O 1s, (C) Ti 2p, (D) Al 2p measured at a 60° emission angle.

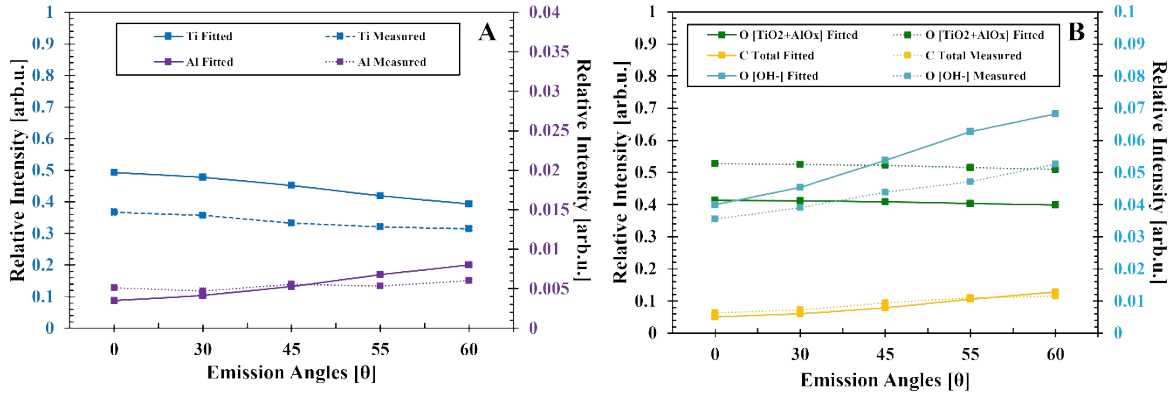

Figure S3: Variation in the ARXPS intensity of measured elements C, O, Ti, and Al versus the emission angles, solid lines connect the fitted intensity ratios, and the dashed lines connect the relative intensity of the measured data for the sample with deposition.

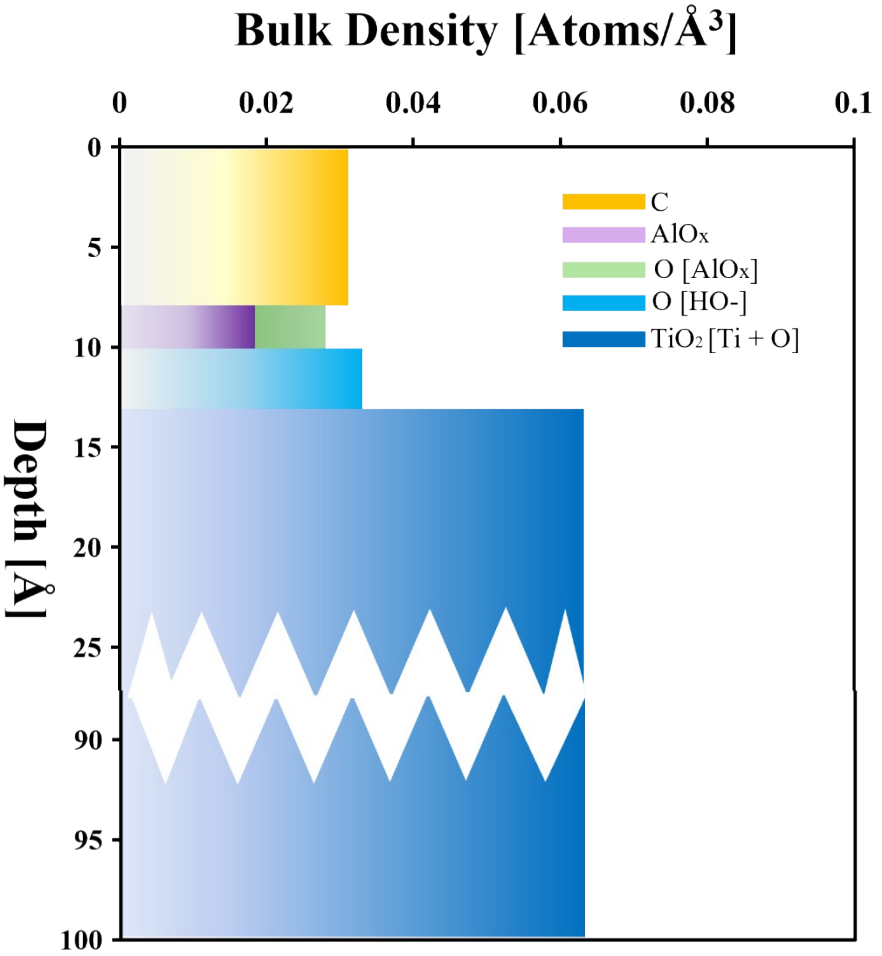

Figure S4: The concentration depth profile of the 1 ALD Cycle sample. The model presents the atomic densities of each emitting constituent element versus the depth in Angstrom (Å) within each respective layer.

5 ALD Cycle results (ARXPS)

The XP spectra of the four elements detected for high-resolution is presented in the main manuscript at a 0° emission angle. Figure S6. Shown the high-resolution of C 1s, O 1s, Ti 2p, and Al 2p at a 60° emission angle.

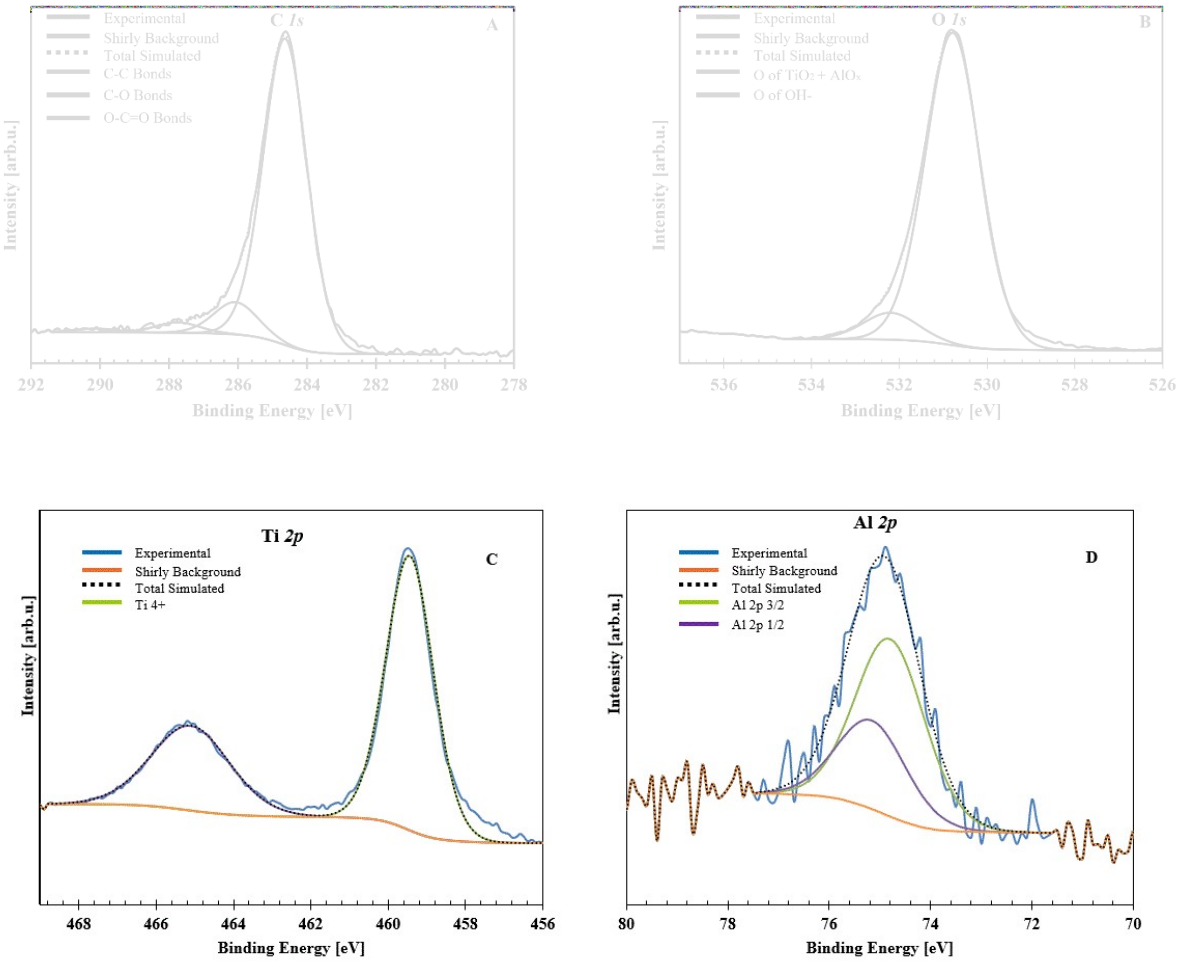

Figure S5: High-resolution XP spectra of 5 ALD-AlO_x deposited onto RF-sputtered TiO_2, fitted with a Shirley background, representing the respective elements of (A) C 1s, (B) O 1s, (C) Ti 2p, (D) Al 2p measured at a 60° emission angle.

10 ALD Cycle results (ARXPS)

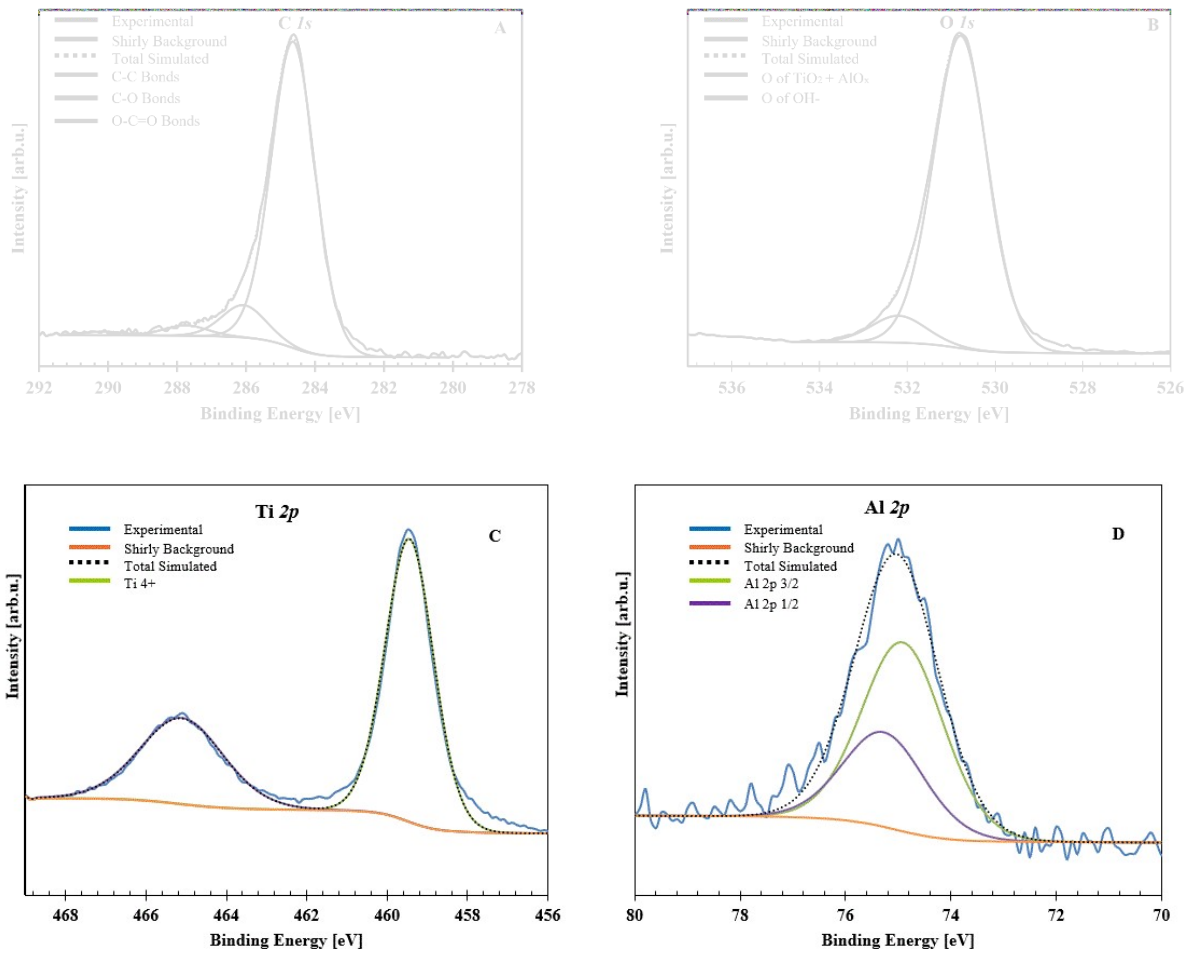

Figure S6: High-resolution XP spectra of 10 ALD-AlO_x deposited onto RF-sputtered TiO_2, fitted with a Shirley background, representing the respective elements of (A) C 1s, (B) O 1s, (C) Ti 2p, (D) Al 2p measured at a 0° emission angle.

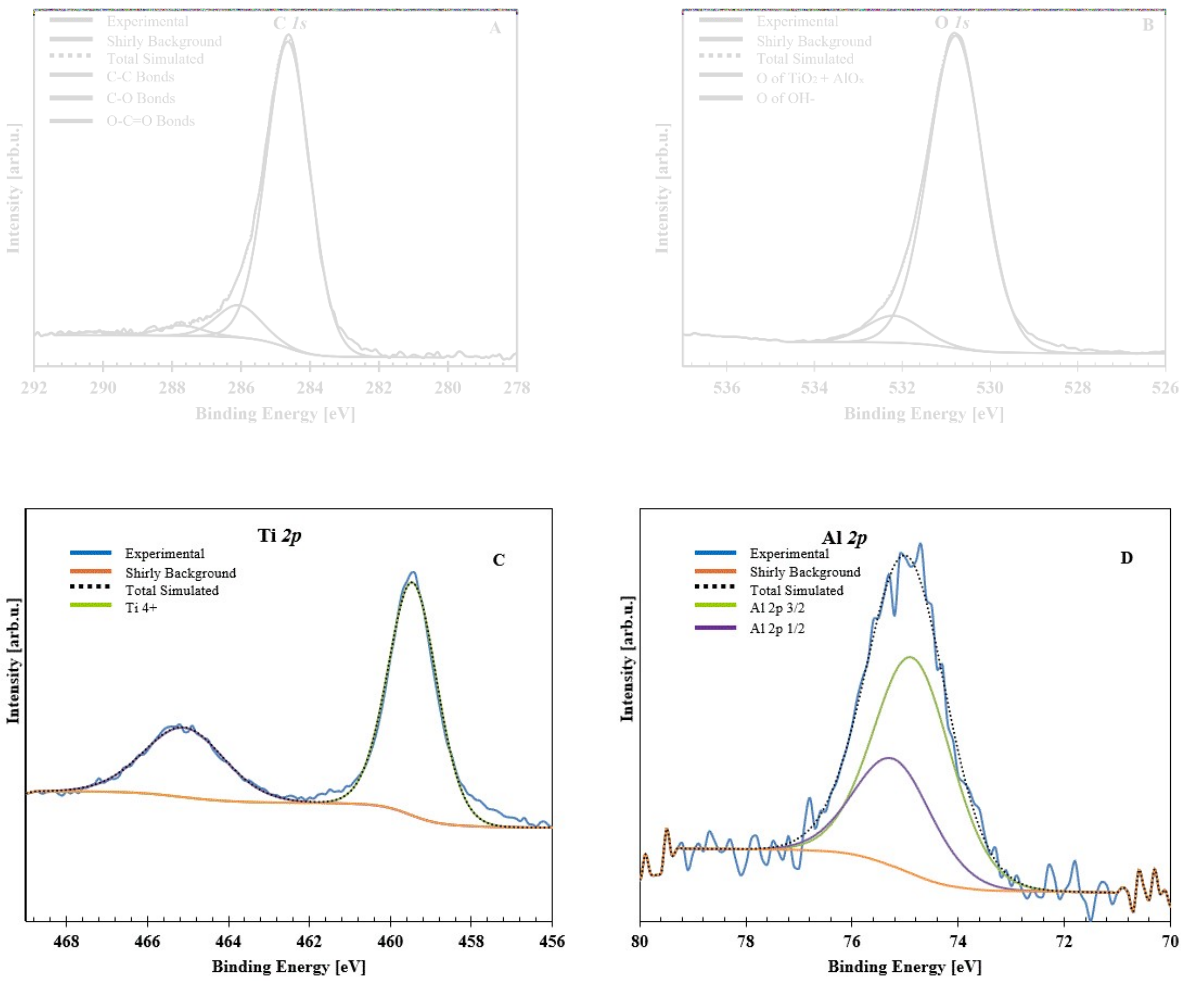

Figure S7: High-resolution XP spectra of 10 ALD-AlO_x deposited onto RF-sputtered TiO_2, fitted with a Shirley background, representing the respective elements of (A) C 1s, (B) O 1s, (C) Ti 2p, (D) Al 2p measured at a 60° emission angle.

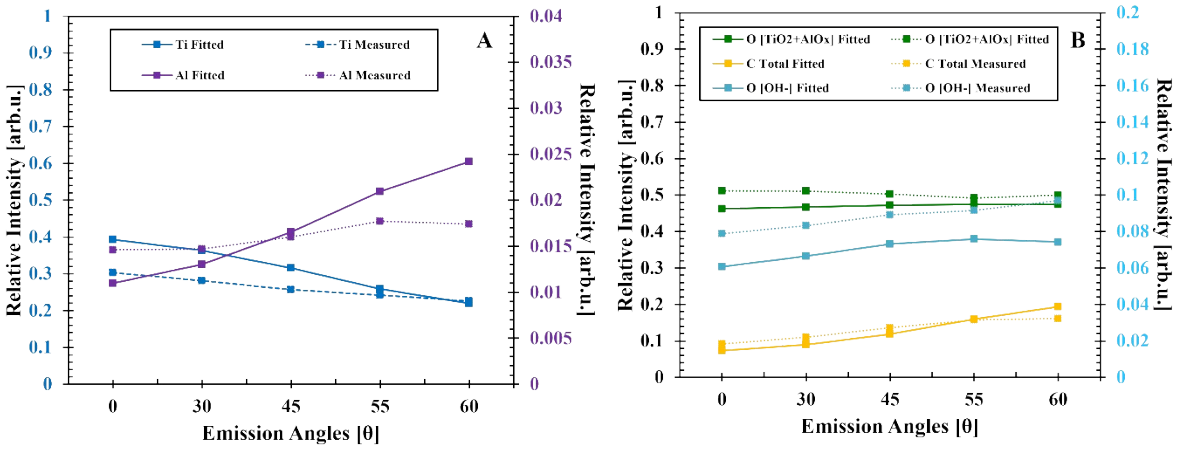

Figure S8: Variation in the ARXPS intensity of measured elements C, O, Ti, and Al versus the emission angles, solid lines connect the fitted intensity ratios, and the dashed lines connect the relative intensity of the measured data for the sample with deposition.

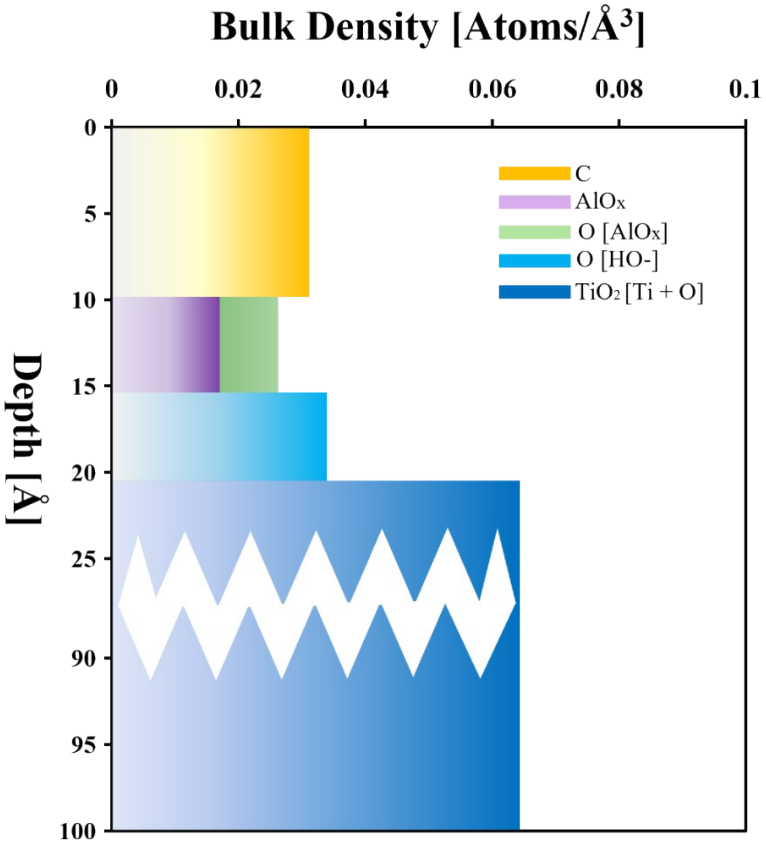

Figure S9: The concentration depth profile of the 10 ALD Cycles sample. The model presents the atomic densities of each emitting constituent element versus the depth in Angstrom (Å) within each respective layer.

XPS Section

Table S4: Peak positions, peak intensity, and elemental composition of sample 1, 5, and 10ALD cycles of Au_{101}/TiO_2 sample.

Sample \ Element		C			O		Ti	Al	Au
		Peak Position			Peak Position		Peak Position	Peak Position	Peak Position
		Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 1	Peak 1	Peak 1
1 ALD Au_{101}/TiO_2	Before ALD	284.4	285.8	287.3	530.5	531.9	459.2	---	83.9
	After ALD	284.3	286.0	289.8	530.5	531.9	459.2	74.3	83.9
5 ALD Au_{101}/TiO_2	Before ALD	284.3	285.7	287.6	530.4	531.9	459.2	---	83.9
	After ALD	284.2	285.5	286.9	530.5	531.9	459.2	74.5	83.9
10 ALD Au_{101}/TiO_2	Before ALD	284.4	285.9	287.4	530.5	531.9	459.2	---	83.9
	After ALD	284.2	285.8	287.6	530.5	531.9	459.2	74.6	83.8
Sample \ Element		C			O		Ti	Al	Au
		Relative intensities			Elemental Composition		Elemental Composition	Elemental Composition	Elemental Composition
		Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 1	Peak 1	Peak 1
1 ALD Au_{101}/TiO_2	Before ALD	10.0	1.6	0.6	58.9	3.6	23.4	---	2.0
	After ALD	9.5	1.7	0.3	56.0	4.0	19.9	6.9	1.7
5 ALD Au_{101}/TiO_2	Before ALD	7.2	1.2	0.3	60.9	4.0	24.1	---	2.3
	After ALD	7.7	1.6	0.5	52.7	8.4	16.8	10.5	1.9
10 ALD Au_{101}/TiO_2	Before ALD	7.9	0.9	0.4	60.9	3.6	24.2	---	2.1
	After ALD	9.8	2.1	0.6	45.3	13.6	11.9	15.5	1.4

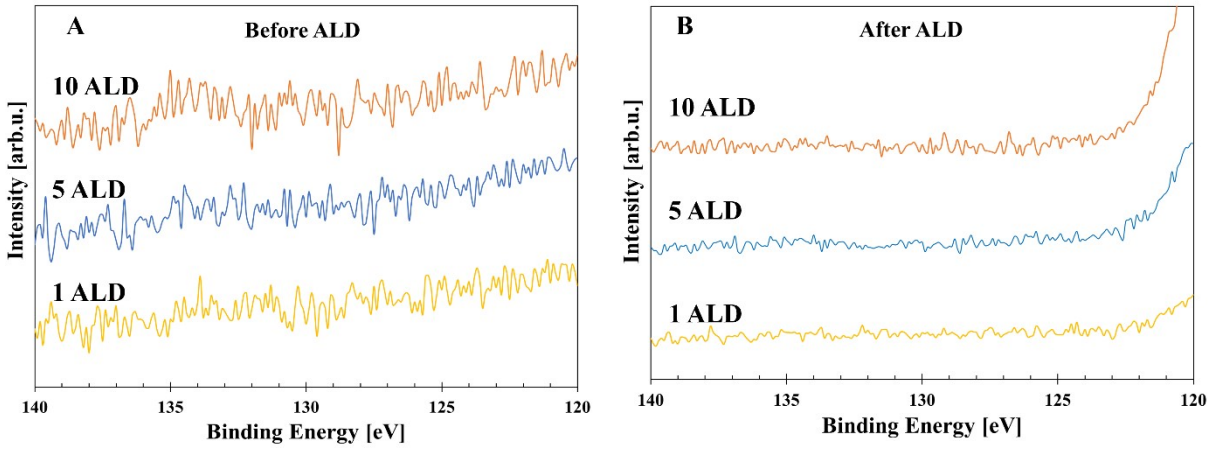

Figure S10: The high-resolution spectra of P 2p of the phosphine ligands (A) before ALD, and (B) after ALD of 1, 5, and 10 ALD cycles.

ISS Section

For converting the sputtering dose into depth, it needs to be taken into account that during the sputtering process also material from the rest gas of the vacuum chamber is adsorbing onto the surface. Thus, the sum of sputtered material is the material sputtered from the sample as such plus the amount of gas adsorbing onto the surface of the sample during the sputtering process. The adsorption during sputtering has to be taken into account for a UHV pressure of a few 10^{-10} mbar and depends on the composition of the UHV rest gas and the sticking coefficient of the gas molecules reaching the sample surface. The amount of material adsorbing onto the surface depends on the sticking coefficient of the surface and is significantly higher for an inorganic surface such as AlO_x, Au and TiO_2 compared to a surface formed by hydrocarbons. The adsorption process is self-limiting in UHV because sticking of hydrocarbons and water is significantly reduced once the first layer has adsorbed from the rest gas. During sputtering this layer is removed making the surface more susceptible to fresh adsorption.

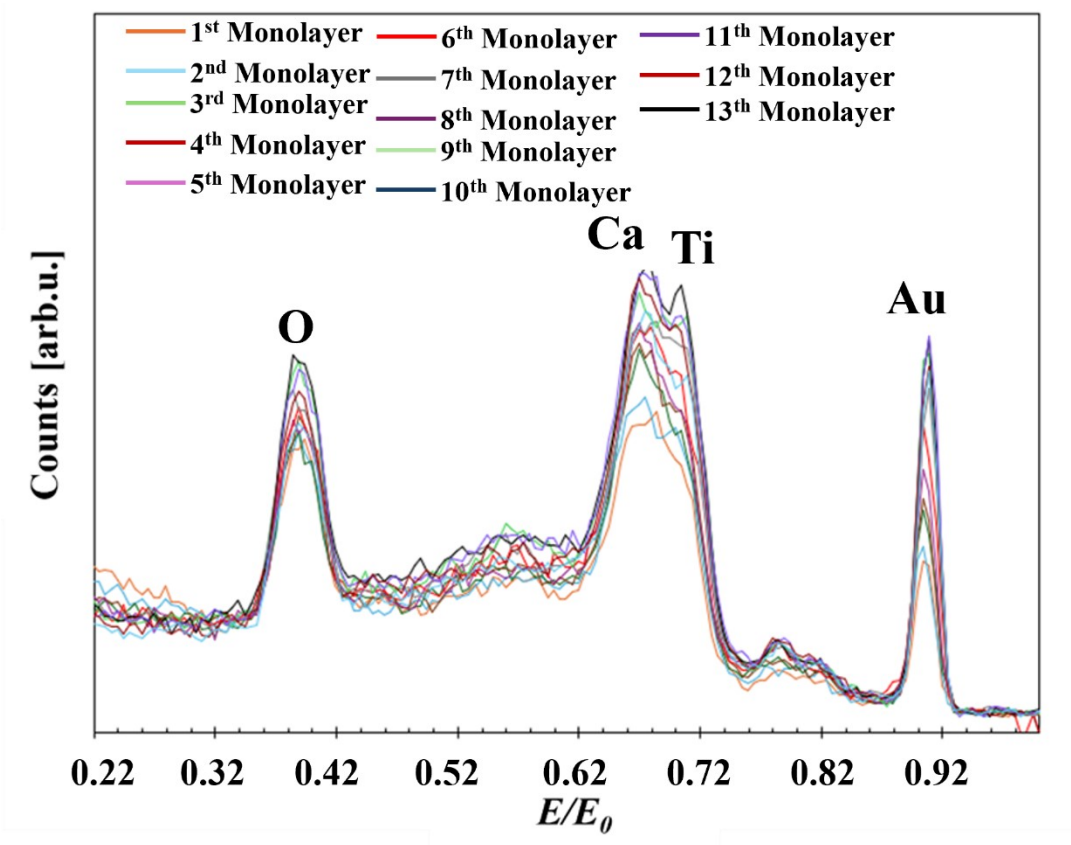

Figure S11: ISS survey spectra for Au_{101}/TiO_2 sample. In the legend the number of sputtered monolayers is shown.

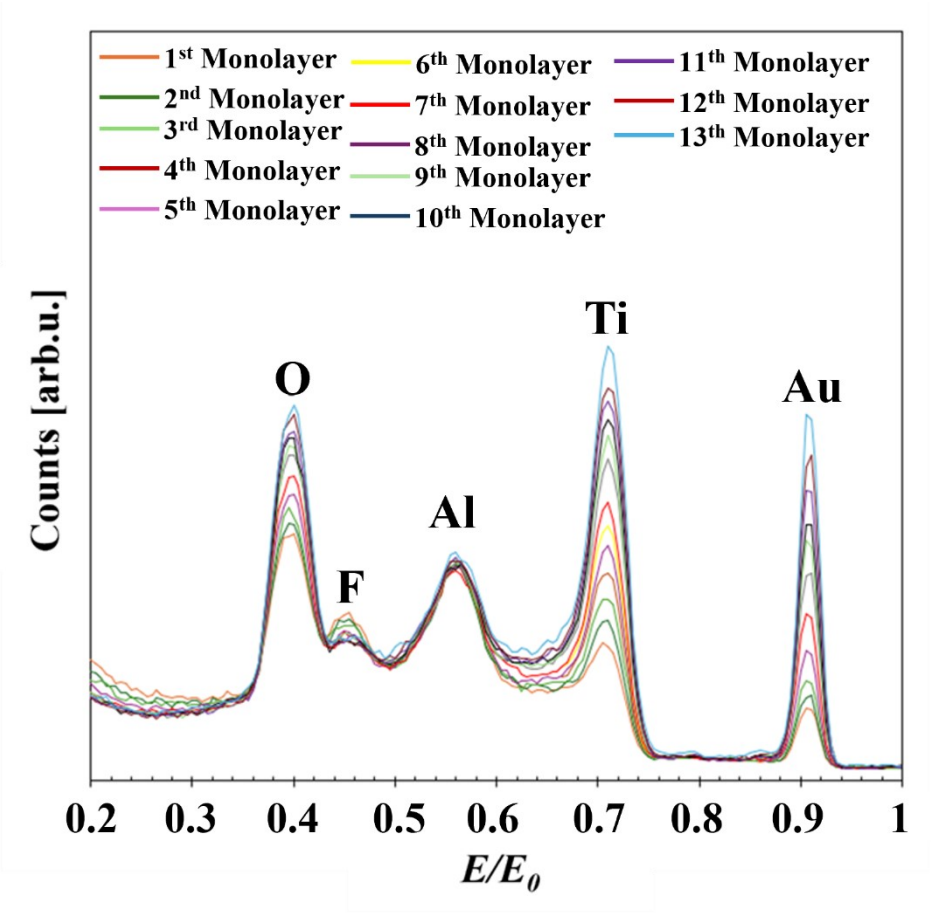

Figure S12: ISS survey spectra for5 ALD $AlO_x/Au_{101}/TiO_2$ sample.

ISS Monolayer Calculations

To convert the number of ISS scans (total number of scans 75) to sputtered monolayers we applied the following procedure,

The ion irradiation *irr* in C for a single scan is calculated as the product of the ion current per area times the time of the scan.

$$irr = t \cdot I = 34\text{s} \cdot 0.16 \cdot 10^{-9}\, A/mm^2 = 5.4 \cdot 10^{-6}\, C \ldots .eq.2$$

The total number of ions hitting the sample per scan is the irradiation divided by the elementary charge e.

$$Total\ No\ of\ Ions\ (hitting\ the\ sample\ per\ scan) = \frac{irr}{e} = \frac{5.4 \cdot 10^{-6}\, C}{1.60 \cdot 10^{-19} C} = 3.4x10^{13} \ldots .eq.3$$

The ion dose is the number of ions per unit area that the ions hit. The area corresponding to the diameter of the ion beam is approximately 1 mm^2.

$$Total\ of\ Ions\ Dose = \frac{Total\ Number\ of\ Ions}{Area} = \frac{3.4{\cdot}10^{13}}{1{\cdot}10^{-2}cm^2} = 3.4{\cdot}10^{15} Ions/cm^2 ...eq.4$$

The sputter efficiency is a measure for how many sample atoms can be removed by a single projectile hitting the sample surface. In case of He a reasonable approximation is a sputter efficiency of 0.1 which means that approximately 10 He projectile remove one atom forming the sample.

The number of sputtered monolayers is calculated as

$$Number\ of\ sputtered\ Monolayers = \frac{Total\ ion\ dose{\cdot}sputter\ efficiency}{Atoms\ per\ monolayer} ....eq.5$$

The number of atoms per monolayer is the number of atoms per unit cell divided by the area of the unit cell.

Al_2O_3: $\#\ atoms/monolayer = \frac{30}{(4.75{\cdot}10^{-8}\ cm)^2} = 1.3{\cdot}10^{16}\ atoms/cm^2 ....eq.6$

The height of a Al_2O_3 monolayer is 11.4 Ang assuming a cubic structure.

TiO_2: $\#\ atoms/monolayer = \frac{6}{(4.6{\cdot}10^{-8}\ cm)^2} = 2.8{\cdot}10^{15} atoms/cm^2 ....eq.7$

The height of a TiO_2 monolayer is 2.96 Å assuming a tetragonal rutile structure.

Au: $\#\ atoms/monolayer = \frac{4}{(4.08{\cdot}10^{-8}\ cm)^2} = 1.7{\cdot}10^{15} atoms/cm^2 ....eq.8$

The height of a Au monolayer is 4.078 Å assuming a fccit structure.

The unit cell parameters are

α-Al_2O_3: a = b = 4.75 Å, c = Å

Rutile TiO_2: a = b = 4.59 Å, c = 2.96 Å

Au: a = b = c = 4.078 Å

The number of sputtered monolayers is thus:

Al_2O_3: $\frac{3.4x10^{14}}{1.3{\cdot}10^{16}} = 2.6x10^{-2}\ monolayers/scan$

TiO_2: $\frac{3.4x10^{14}}{2.8{\cdot}10^{15}} = 1.2x10^{-1}\ monolayers/scan$

Au: $\frac{3.4x10^{14}}{1.7{\cdot}10^{15}} = 1.9x10^{-1}\ monolayers/scan$

NICISS Section

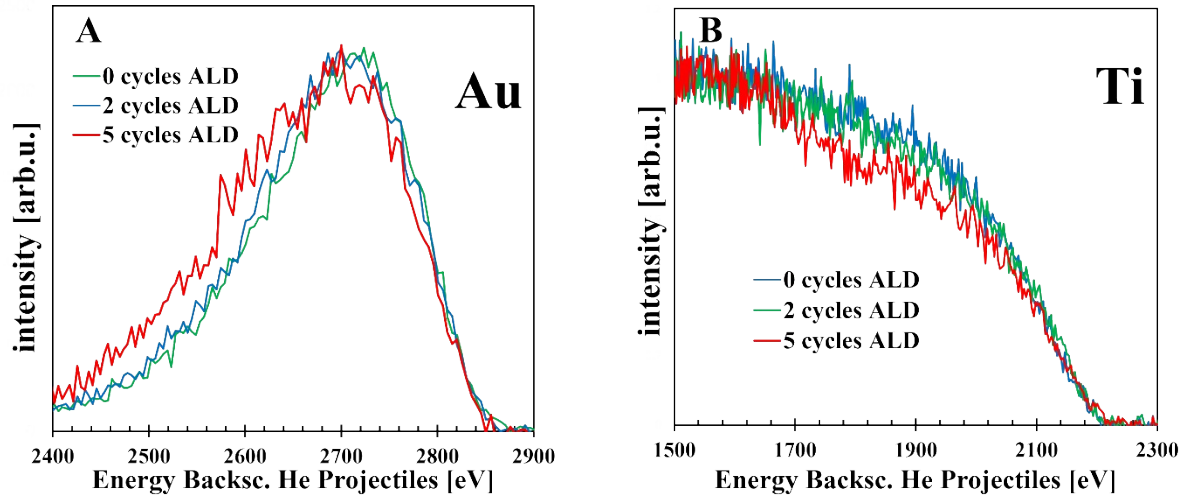

Figure S13: (A) NICIS spectra of gold and gold coated with 2 and 5 cycles of ALD-AlO_x (B) NICIS spectra of titanium without ALD, with 2 and 5 cycles of ALD-AlO_x.

Determining the position of O of AlO_x in XPS

A Si wafer 1 cm^2 coated with 50 nm of Au was coated with AlO_x. Due to the presence of Au the O of SiO_2 cannot be seen in the XP spectra. The O spectra before and after heating to 250 ^0C for removing OH^- from the surface are shown. In A two O peaks and in B a single O peak are found. In A a peak at 531.0 eV corresponding to AlO_x and a peak at 532.2 eV corresponding to OH^- are found. In B a single peak at 531.5 eV corresponding to AlO_x is found.

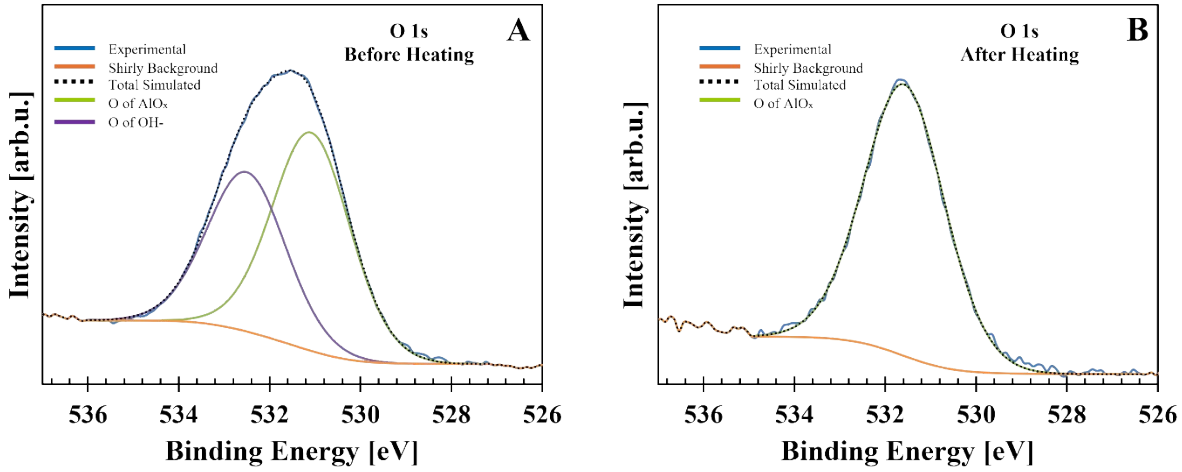

Figure S14: (A) O 1s spectrum for the O fitted with doublet peaks before heating the sample. (B) After heating the O 1s spectrum for the O fitted with a single peak.

Iodine-iodide Exposure Experiment

The Au_{101}/TiO_2 samples with 0, 1, 5, and 10 ALD cycles were exposed to an iodine-iodide solution to test how the Al_2O_3 ALD overlayer can protect the covered Au_{101} clusters against chemical reactions. Each sample wafer was placed in a sealed vial containing 2 mL of an iodine-iodide solution comprising KI (239.3 mg/mL) and I_2 (126.7 mg/mL) in MilliQ water.[4] The samples were exposed for 10 h then removed from the solution and immediately rinsed with MilliQ water and dried under flowing N_2.

Two absorbance peaks in the UV-Vis spectra at 286 and 350 nm related to iodine species were observed for the iodide-iodine solution before exposure (Figure S15). Both peaks decreased significantly after the ALD Au_{101}/TiO_2 samples were exposed to the solution. This indicates that the iodine species had reacted to form complexes such as $[AuI_2]^-$ which do not absorb in these regions.[4]

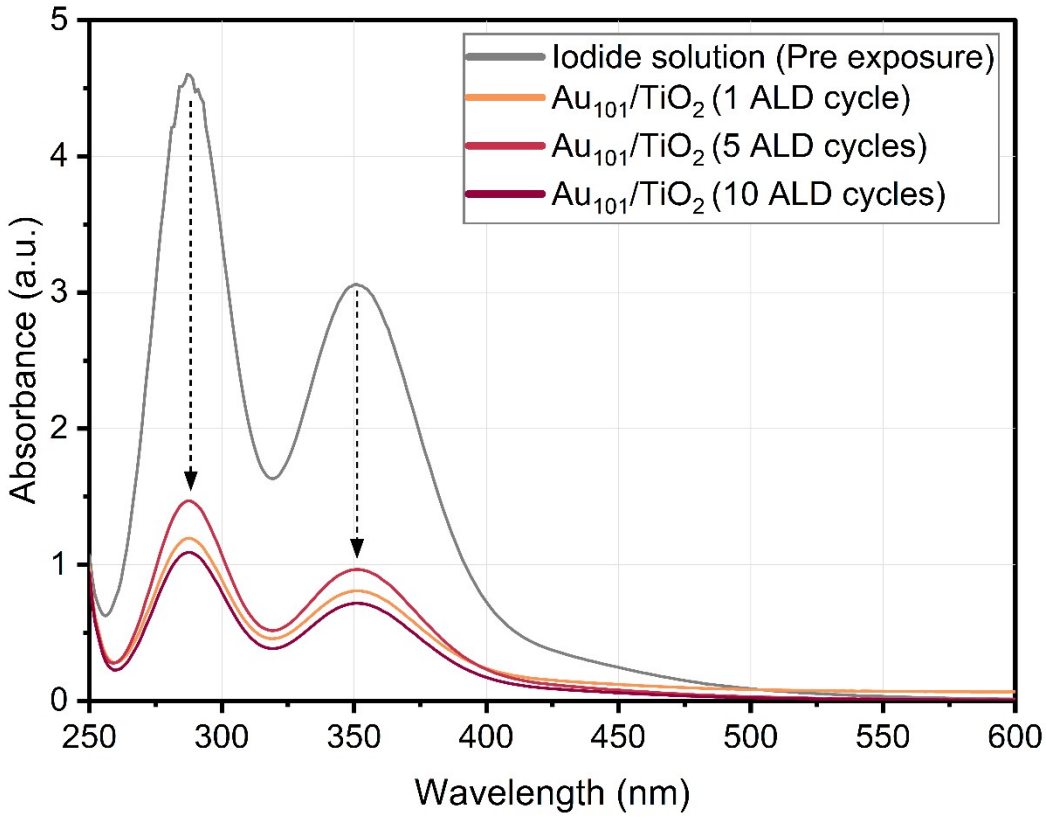

Figure S15: Absorption spectra of the iodine-iodide solution before and after exposure to Au_{101}/TiO_2 with Al_2O_3 overlayer samples for 10 h. Measurements performed with a Cary 3500 UV-Vis spectrophotometer.

Table S5 shows the change in relative intensity of the elements O, Ti, Al and Au representing the substrate, the Au clusters and the Al_2O_3 overlayer. Figure S16 shows the XP spectra of Au

and Al of the 5 ALD on Au_{101}/TiO_2 sample before and after iodine exposure. Before the iodine exposure, a clear Au 4f signal is observed. After iodine exposure, the Au signal intensity decreases significantly and becomes barely distinguishable from the background, indicating that the Au clusters are no longer detectable at the surface. The Al also decreases which could potentially be due to the removal of all Al species which are non-oxide species. While the Au clusters are mostly removed by this treatment, it remains questionable whether such treatment represents the chemical environment during the exposure to H_2O during photocatalysis.

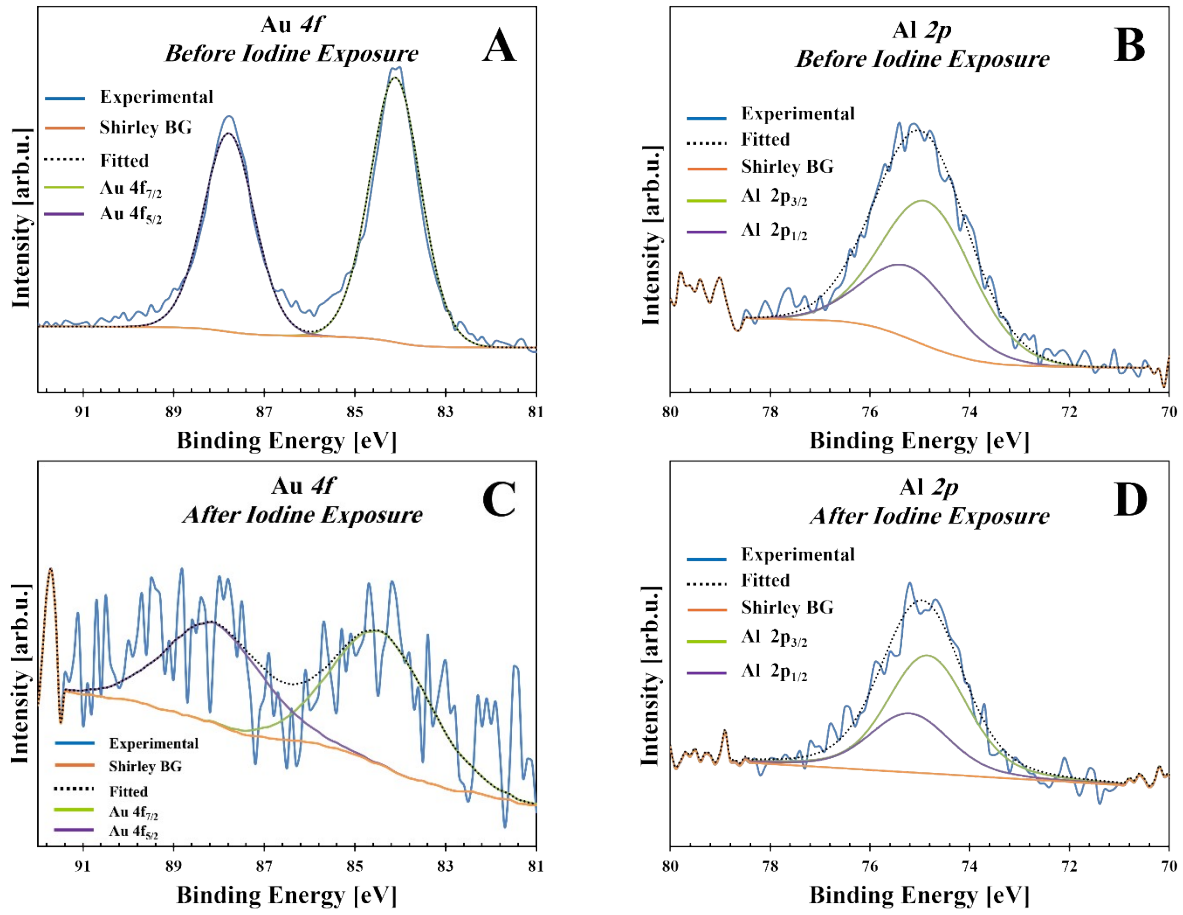

Figure S16: (A) Au 4f spectrum of the sample 5 ALD on Au_{101}/TiO_2 before iodine exposure. (B) Al 2p spectrum before iodine exposure of the sample 5 ALD on Au_{101}/TiO_2. (C) Au 4f spectrum after iodine exposure, and (D) Al 2p spectrum after iodine exposure.

Table S5: Fraction of Al and Au remaining on the TiO_2 surface after applying the iodine procedure. For the calculation only the XPS peaks for the elements forming the substrate have been used, i.e. the O peak at 530.5 eV, the Ti, Al and Au peaks. The other O peaks and C are changing as well but only reflect the surface contamination due to the application of the iodine procedure and are thus not relevant for the analysis.

	XPS Intensity of O, Ti, Al and Au relative to the untreated sample [%]			
	O peak 1 (532.0 eV)	Ti (459.2 eV)	Al (74.7 eV)	Au (84.0 eV)
0 ALD Au_{101}/TiO_2	99	112	-	0
1 ALD Au_{101}/TiO_2	107	107	41	0
5 ALD Au_{101}/TiO_2	107	104	85	5
10 ALD Au_{101}/TiO_2	108	105	68	0

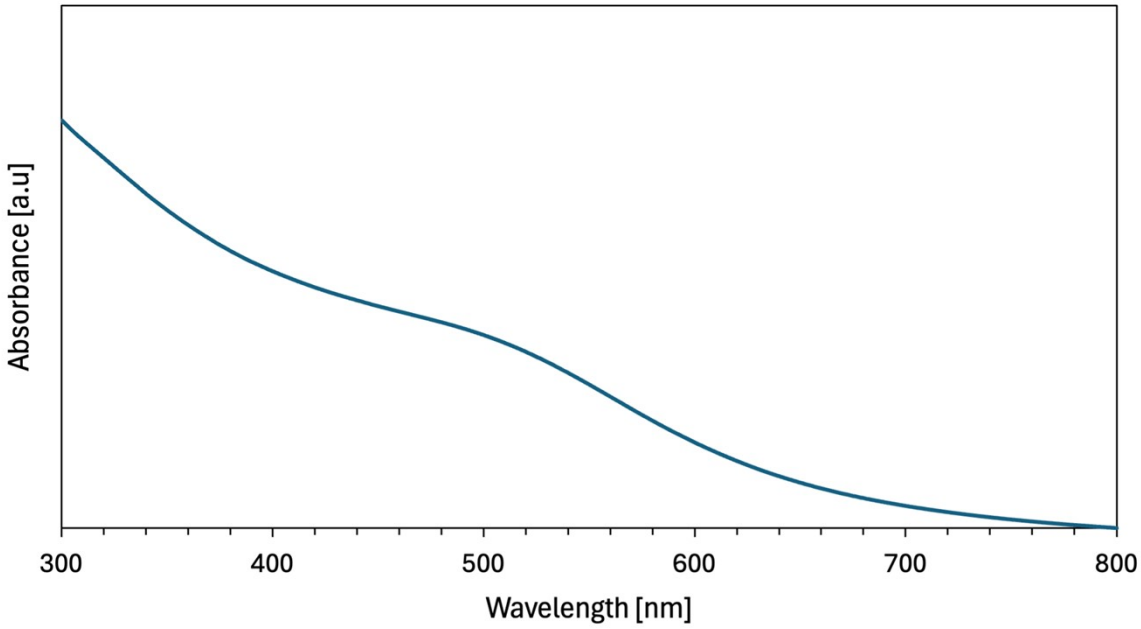

Figure S17: UV-vis absorption spectrum of Au_{101} in dichloromethane.

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