Growth of Single- and Bi-layer ZnO on Au(111) and Interaction with Copper

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Supporting Information

Determining the ZnO stoichiometry from XPS

(1) Simply, the stoichiometry is determined as:

The Zn-to-O ratio = $(I_{Zn3s}/\sigma_{Zn3s}) / (I_{O1s}/\sigma_{O1s})$

where I_{Zn3s} and I_{O1s} refer to the integrated XP intensity, and σ_{Zn3s} and σ_{O1s} are corresponding cross section values obtained from literature.[1] These values are listed in **TableS1**:

Sample	I_{Zn3s}	I_{O1s}	σ_{Zn3s}	σ_{O1s}	Zn:O
ZnO on Au(111)	1786	5728	0.02	0.065	1.01

Thus the oxide is determined to be stoichiometry.

(2) In comparison with the ZnO single crystals

Table S2 lists the intensity ratio of I_{Zn3s} and I_{O1s} for ultrathin ZnO on Au(111), single crystal Zn-ZnO(0001) and O-ZnO(000-1)

Sample	$I_{Zn3s} : I_{O1s}$ (raw data)
Ultrathin ZnO on Au(111)	0.31
Zn-ZnO(0001)	0.42
O-ZnO(000-1)	0.40

Additionally, one needs to take the escape depths of photoelectrons into account for the bulk materials. According to the NIST electron IMFP database, the escape depths of the Zn3s and O1s photoelectrons are 21.6 (KE = 1110 eV) and 15.7 Å (KE = 720 eV) in bulk ZnO, respectively. Based on the exponential escape probability, the corrected $I_{Zn3s} : I_{O1s}$ ratios are listed in **Table S3**:

Sample	$I_{Zn3s} : I_{O1s}$ (corrected)
Ultrathin ZnO on Au(111)	0.31
Zn-ZnO(0001)	0.31
O-ZnO(000-1)	0.29

Clearly, the XP peak ratio of the ultrathin ZnO on Au(111) is in an excellent agreement with that of the stoichiometric single crystals, suggesting that the ultrathin ZnO on Au(111) is also stoichiometry.

Computational benchmark of the influence of U-J value

Table S4: Single-layer ZnO/Au(111)

U-J (eV)	d(O-Zn)(Å)	d(Zn-Au) (Å)	E_{ad}(ZnO-Au) (eV)
8.5	0.10	2.64	0.43
4.7	0.11	2.63	0.42

Table S5: Bi-layer ZnO/Au(111)

U-J (eV)	d(O-Zn) (Å)	d(Zn-Zn)(Å)	d(Zn-Au) (Å)	E_{ad}(ZnO-ZnO)(eV)
8.5	0.06	2.09	2.76	0.95

4.7	0.04	2.22	2.78	0.78

Computational benchmark of the dependence on the Au(111) slab thickness

Table S6: Single-layer ZnO/Au(111)

Au(111)	d(O-Zn)(Å)	d(Zn-Au) (Å)	E_{ad}(ZnO-Au) (eV)
three-layer	0.10	2.64	0.43
four-layer	0.10	2.65	0.44
five-layer	0.09	2.63	0.45

Table S7: Bi-layer ZnO/Au(111)

Au(111)	d(O-Zn) (Å)	d(Zn-Zn)(Å)	d(Zn-Au) (Å)	E_{ad}(ZnO-ZnO)(eV)
three-layer	0.06	2.09	2.76	0.95
four-layer	0.06	2.11	2.73	0.93
five-layer	0.06	2.09	2.74	0.93

For structure with three-layer thick Au(111) slab, ZnO and top most Au layers were allowed to relax. For structure with four-layer thick and five-layer thick Au(111) slab, ZnO and top two Au layers were allowed to relax.

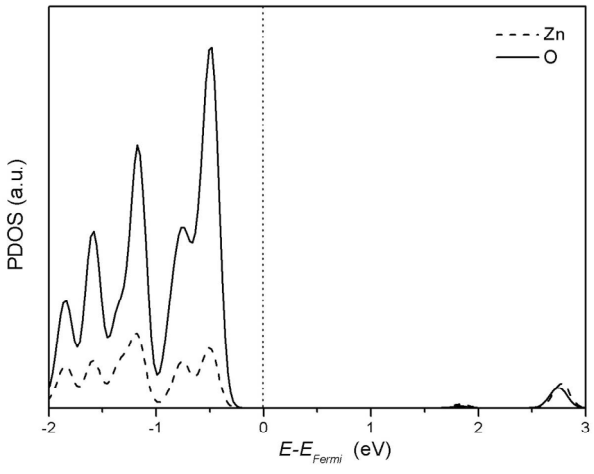

Figure S1. PDOS of the unsupported single-layer ZnO with the same predistorted structure as the supported one. A band gap of more than 1.5 eV can be clearly seen.

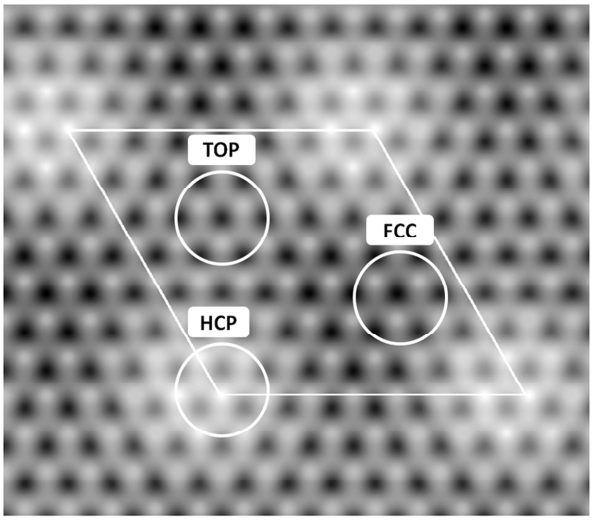

Figure S2. Simulated STM image of supported single-layer ZnO at a bias of 1.5 eV. The contrast differences between the domains can be better seen.

Reference

1. Yeh, J. J.; Lindau, I., Atomic Subshell Photoionization Cross-Sections and Asymmetry Parameters (1 <= Z <= 103). *Atom. Data Nucl. Data Tables* **1985,** *32* (1), 1-155.