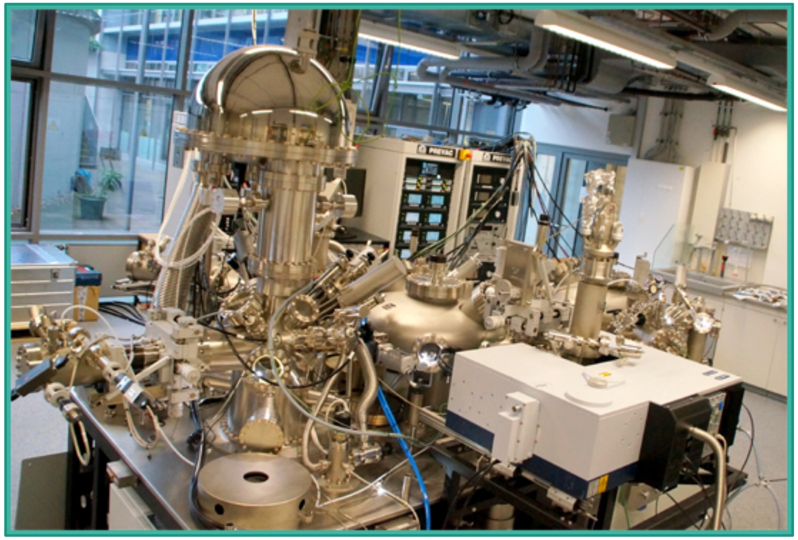
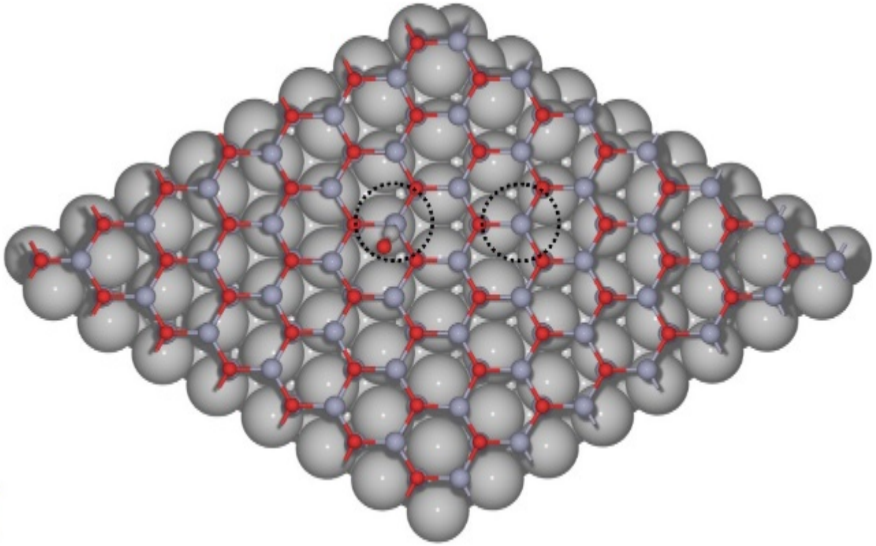
Karlsruhe Institute of Technology

IRRAS and DFT Investigations of Ultrathin ZnO Films Formed on Ag(111)

Xiaojuan Yu, Mie Andersen, Alexei Nefedov, Karsten Reuter, Christof Wöll and Yuemin Wang

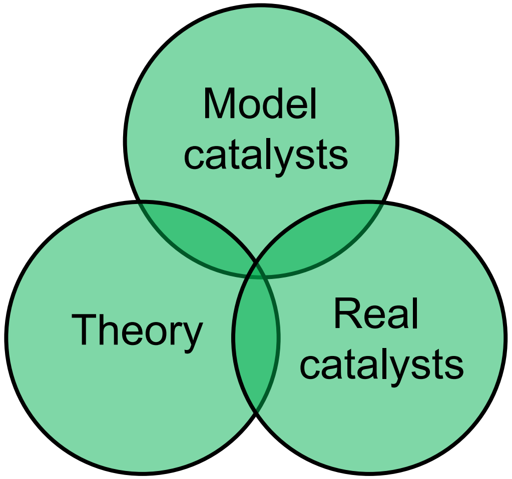
Institute of Functional Interfaces (IFG)





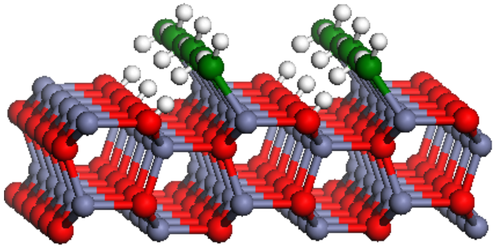
"Surface Science" approach to heterogeneous catalysis

- Fundamental understanding of nanostructured catalysts based on comprehensive reference data acquired for model systems

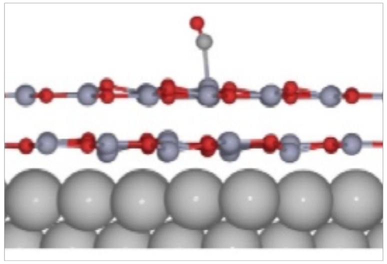


Prof. Gerhard Ertl
The Nobel Prize winner in Chemistry 2007

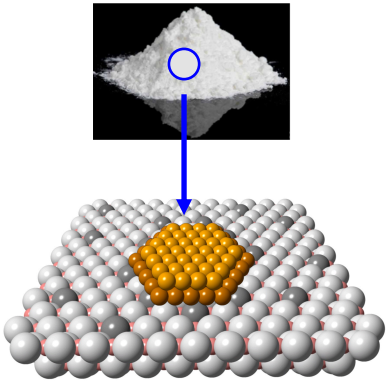
water on ZnO(10-10) single-crystal surfaces



CO on ZnO thin films

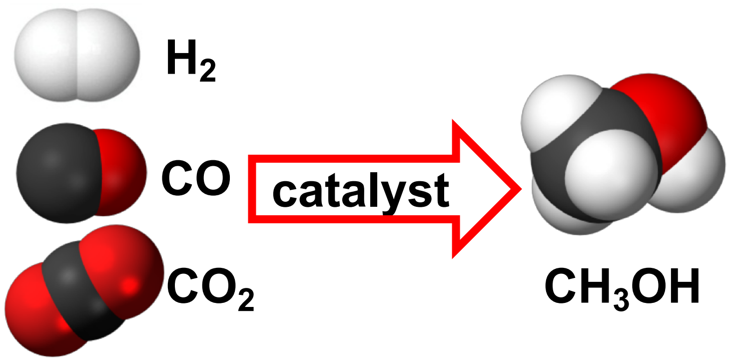


Cu/CeO_2 Nanoparticles



Metal oxide thin films

Catalyst : Cu/ZnO/Al_2O_3

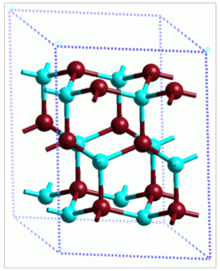


Catalyst : Cu/ZnO/Al_2O_3

S. Kuld et al., Science. 2016, 352, 969.

M. Behrens et al., Science. 2012, 336, 893.

wurtzite

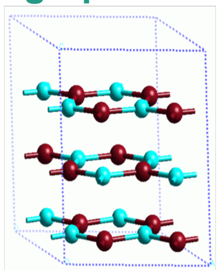


ZnO thin films

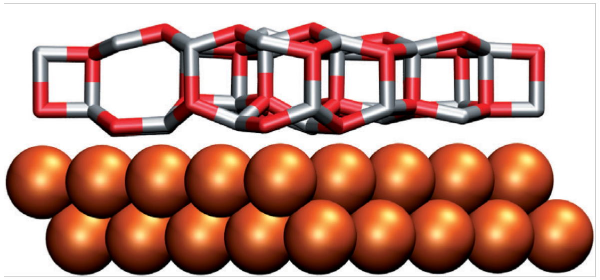
S. Tusche et al., Phys. Rev. Lett. 2007, 99, 026102.

C. L. Freeman et al., Phys. Rev. Lett. 2006, 96, 066102.

graphitic

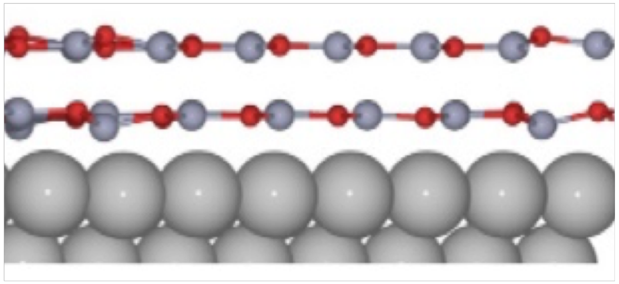


IRRAS: ZnO/Cu(111)



V. Schott, et al., Angew. Chemie, Int. Ed. 2013, 52, 11925

IRRAS: ZnO/Ag(111)



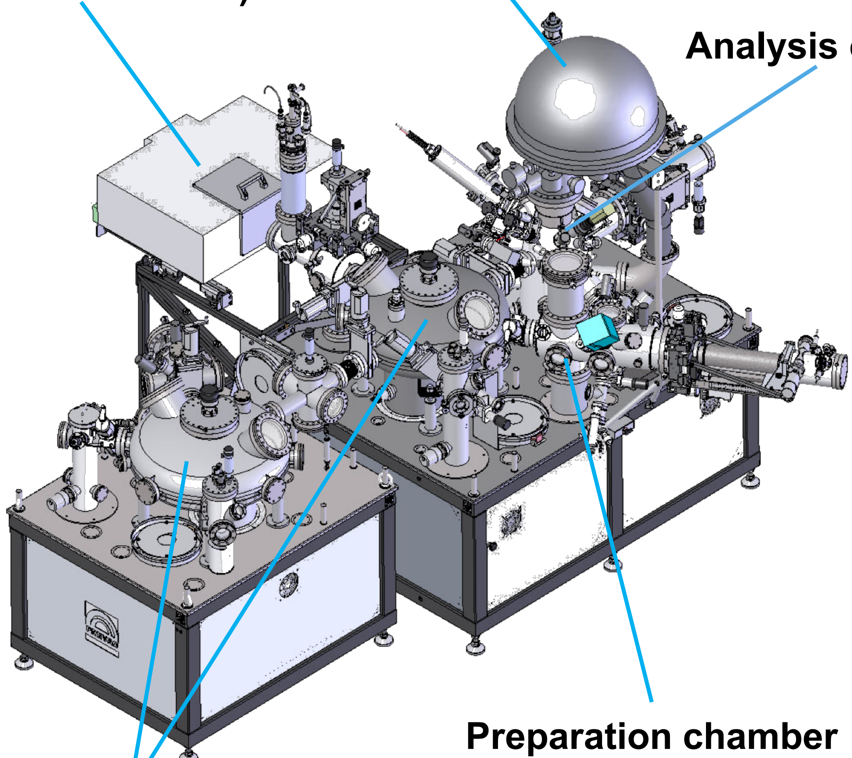
M. Andersen, X. Yu, et al., J. Phys. Chem. C 2018, 122, 4963

UHV-FTIR apparatus "THEO"

UHV-FTIR
(Bruker Vertex 80v)

XPS, UPS and AES analyzer
(VG Scienta R4000)

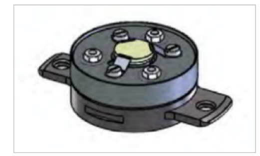
Analysis chamber

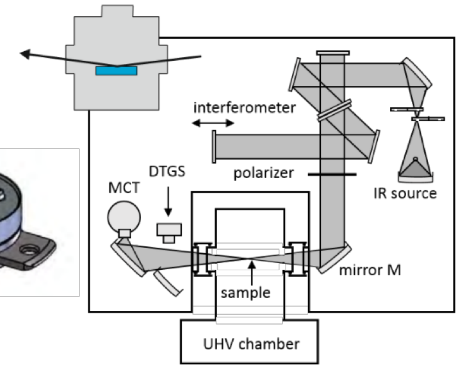


Distribution chambers

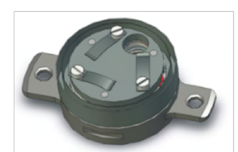
Preparation chamber
with LEED, AES, TDS
and effusion cells

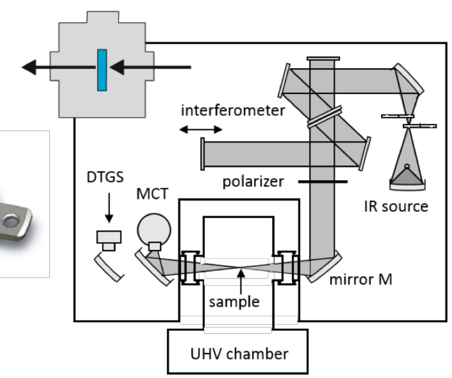
- Single crystals
- Supported thin films
- Nanoparticles





Polarization-resolved IRRAS
on flat model catalysts

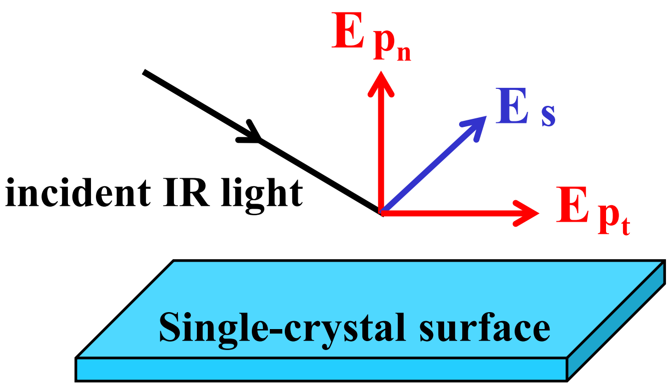




Temperature-dependent and time-
resolved transmission
measurements on real catalysts

Y. Wang, C. Wöll, Chem. Soc. Rev., 2017, 46, 1875.

Infrared reflection-absorption spectroscopy (IRRAS)

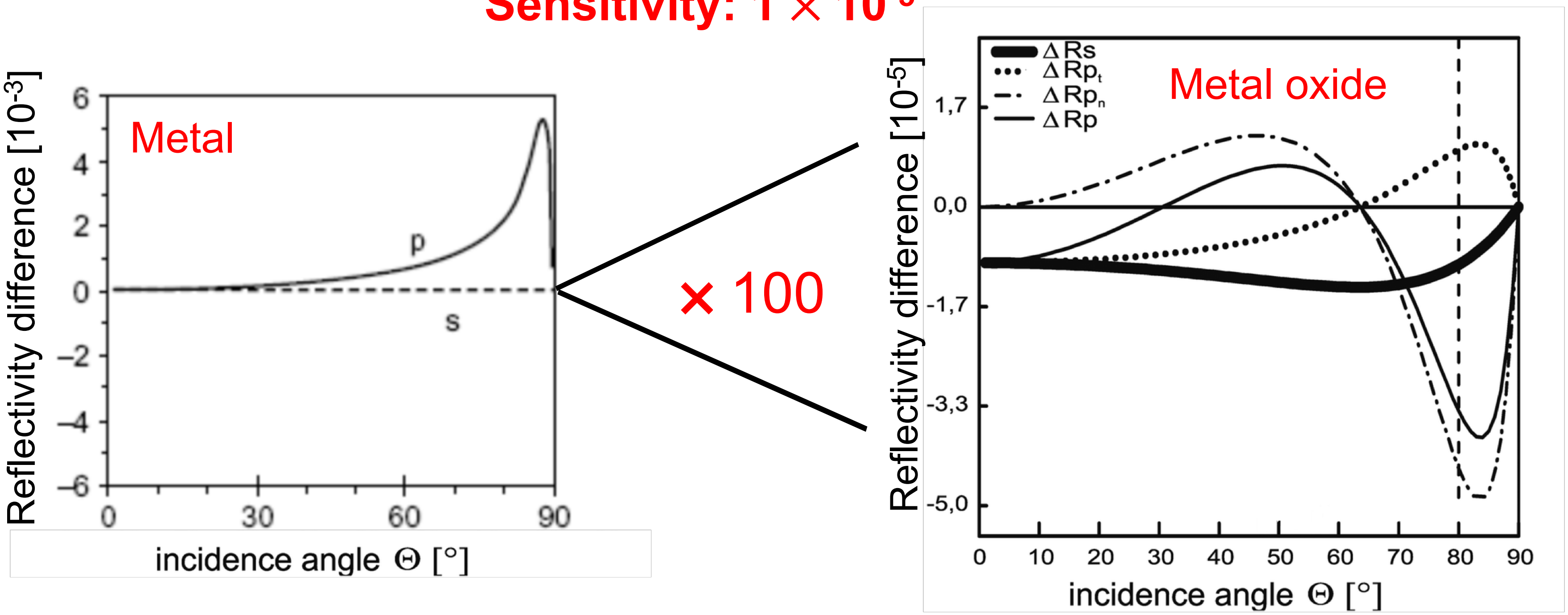


$$\Delta A_s(\theta) = -\frac{16\pi}{\ln 10}\left[\frac{\cos\theta}{n_3{}^2 - 1}\right]\frac{n_2 k_2 d_2}{\lambda}$$

$$\Delta A_{pt}(\theta) = -\frac{16\pi}{\ln 10}\left[\frac{\cos\theta}{\frac{\xi_3{}^2(\theta)}{n_3{}^4} - \cos^2\theta}\right]\left[-\frac{\xi_3{}^2(\theta)}{n_3{}^4}\right]\frac{n_2 k_2 d_2}{\lambda}$$

$$\Delta A_{pn}(\theta) = -\frac{16\pi}{\ln 10}\left[\frac{\cos\theta}{\frac{\xi_3{}^2(\theta)}{n_3{}^4} - \cos^2\theta}\right]\frac{\sin^2\theta}{(n_2{}^2 + k_2{}^2)^2}\frac{n_2 k_2 d_2}{\lambda}$$

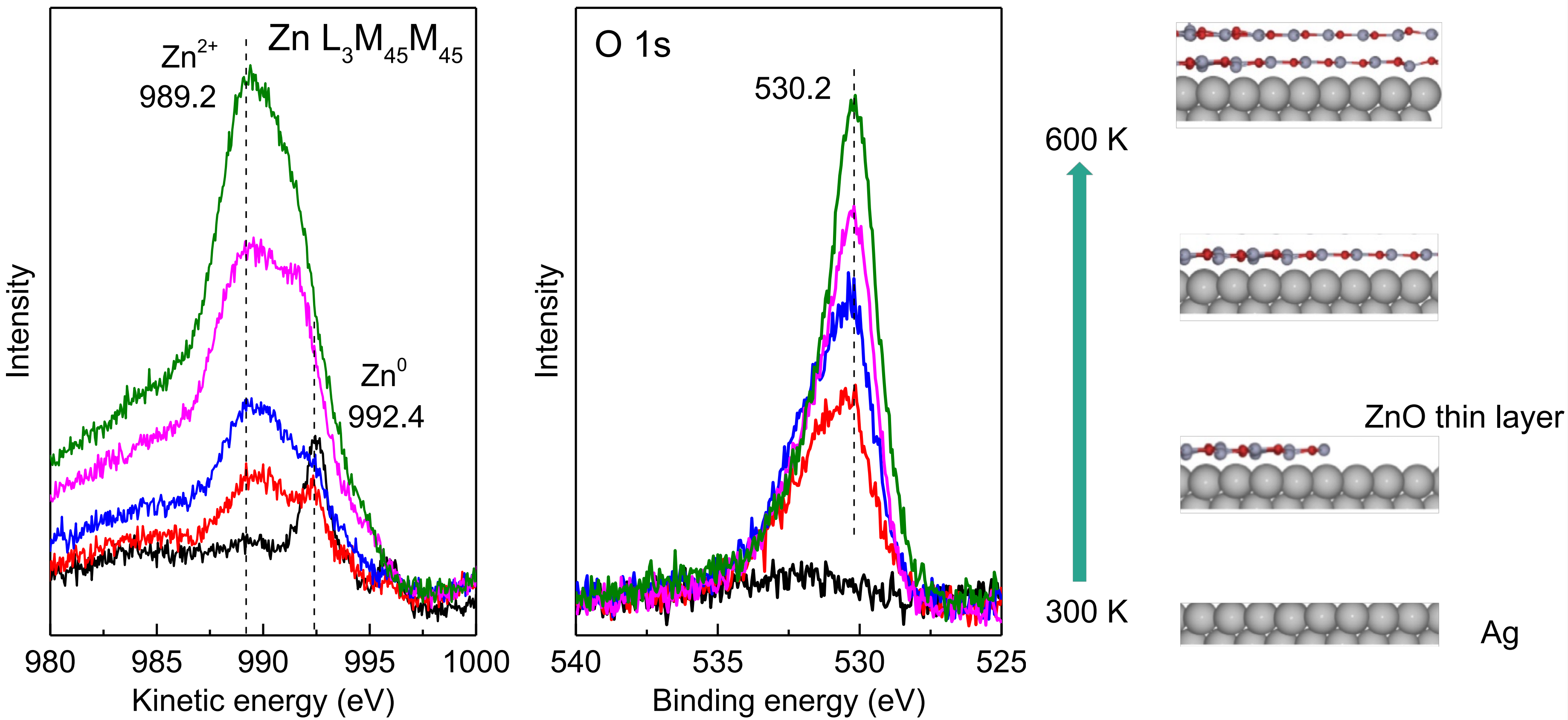
Sensitivity: 1×10^{-5}



Y. Wang, C. Wöll, Chem. Soc. Rev., 2017, 46, 1875.

ZnO/Ag(111): growth of ZnO thin films monitored by XPS

Grazing angle $\boldsymbol{\theta = 70°}$



Increase of the surface Zn concentration due to the formation of ZnO thin films

M. Andersen, X. Yu, et al., *J. Phys. Chem. C* 122 (2018), 4963−4971.

ZnO/Ag(111): growth of ZnO thin films monitored by XPS

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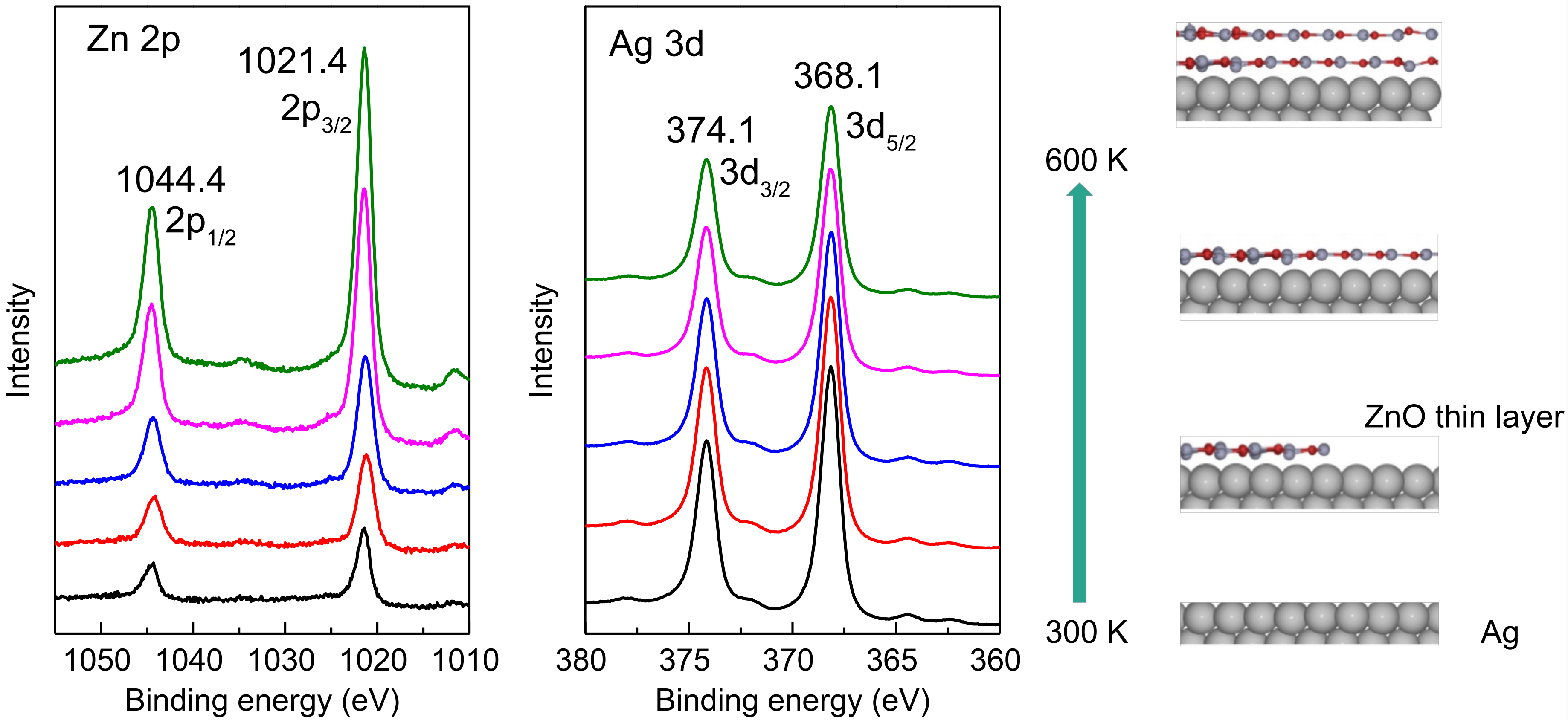


Increase of the surface Zn concentration due to the formation of ZnO thin films

M. Andersen, X. Yu, et al., *J. Phys. Chem. C* 122 (2018), 4963−4971.

ZnO/Ag(111): thickness of ZnO thin films

$$\frac{I_A}{I_S} = \frac{T_A \sigma_A n_A \lambda_A(E_A)}{T_S \sigma_S n_S \lambda_S(E_S)} \cdot \frac{1 - e^{-\frac{d}{\lambda_A(E_A)\cdot\cos(\theta)}}}{e^{-\frac{d}{\lambda_A(E_S)\cdot\cos(\theta)}}}$$

S. V. Merzlinkin et al., Surf. Sci. 2008, 602, 755-767

The atomic density of ZnO

wurzite – 4.89 × 10^{-2} atoms/Å^3, graphitic – 4.08 × 10^{-2} atoms/Å^3.

F. Claeyssens et al., J. Mater. Chem. 2005, 15, 139-148. C. L. Freeman et al., Phys. Rev. Lett. 2006, 96, 066102.

Oxidation with O_2 at 600K for 10 min: 1.9 Å (assuming graphitic-type ZnO) ⇨ 1 ML

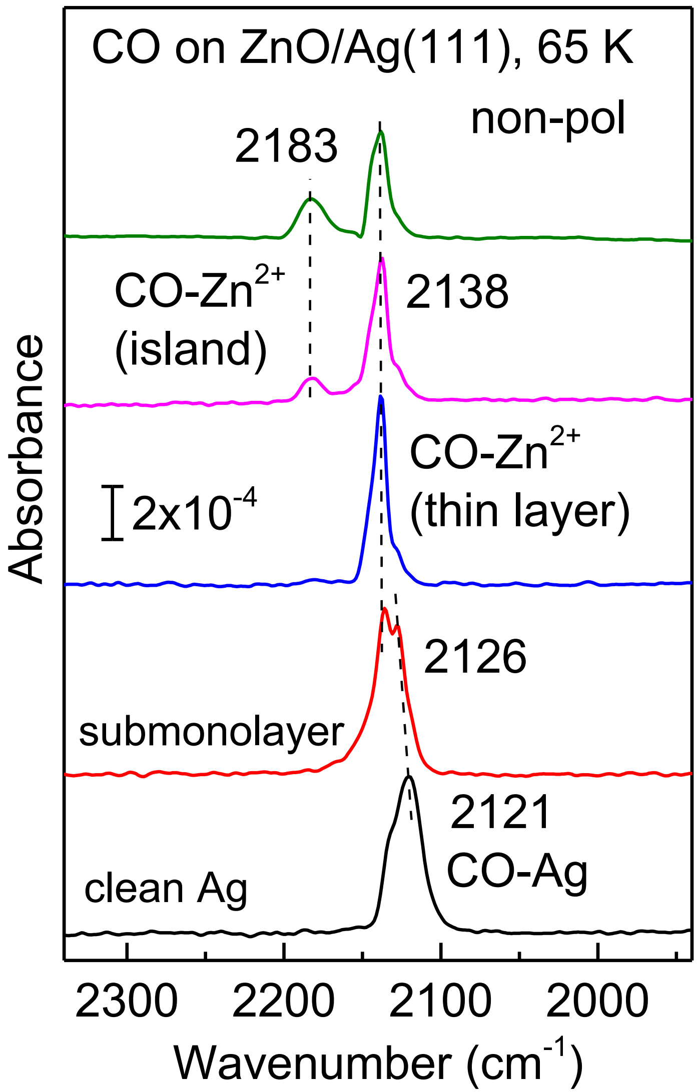
20 min: 3.4 Å (assuming graphitic-type ZnO) ⇨ 2 ML

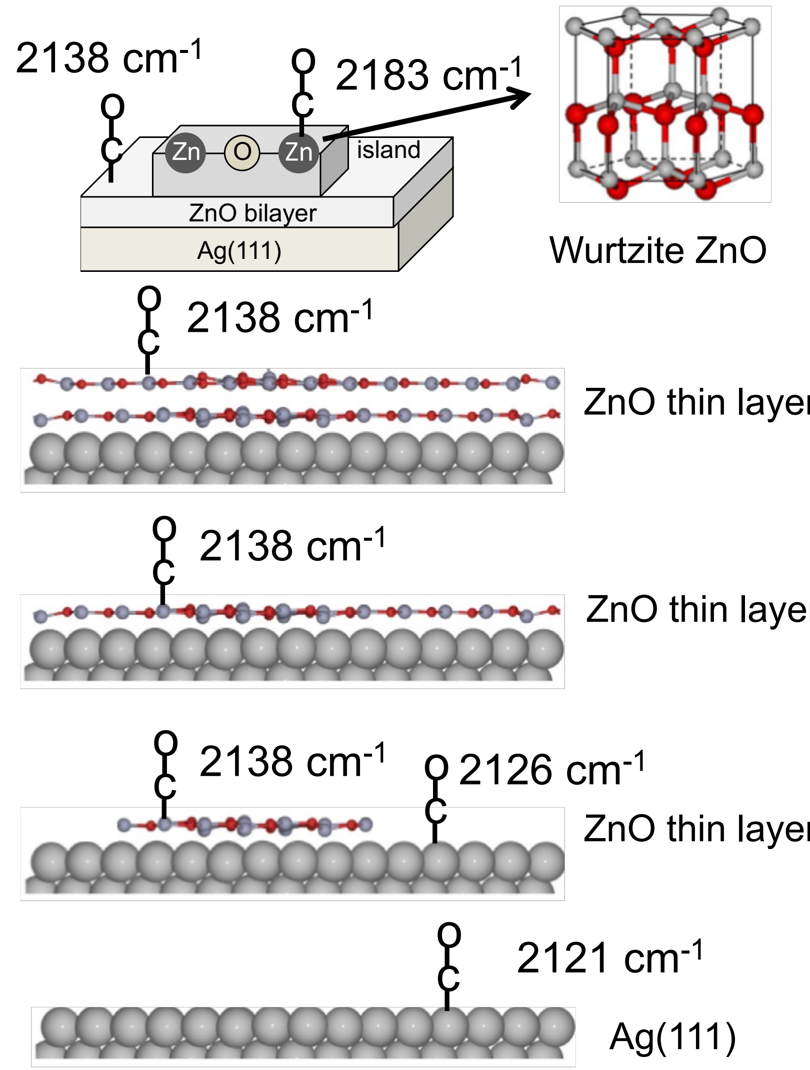
40 min: 4.4 Å (assuming graphitic-type ZnO)

or 3.7 Å (assuming wurztite-type ZnO) ⇨ 3-4 ML

M. Andersen, X. Yu, et al., *J. Phys. Chem. C* 122 (2018), 4963−4971.

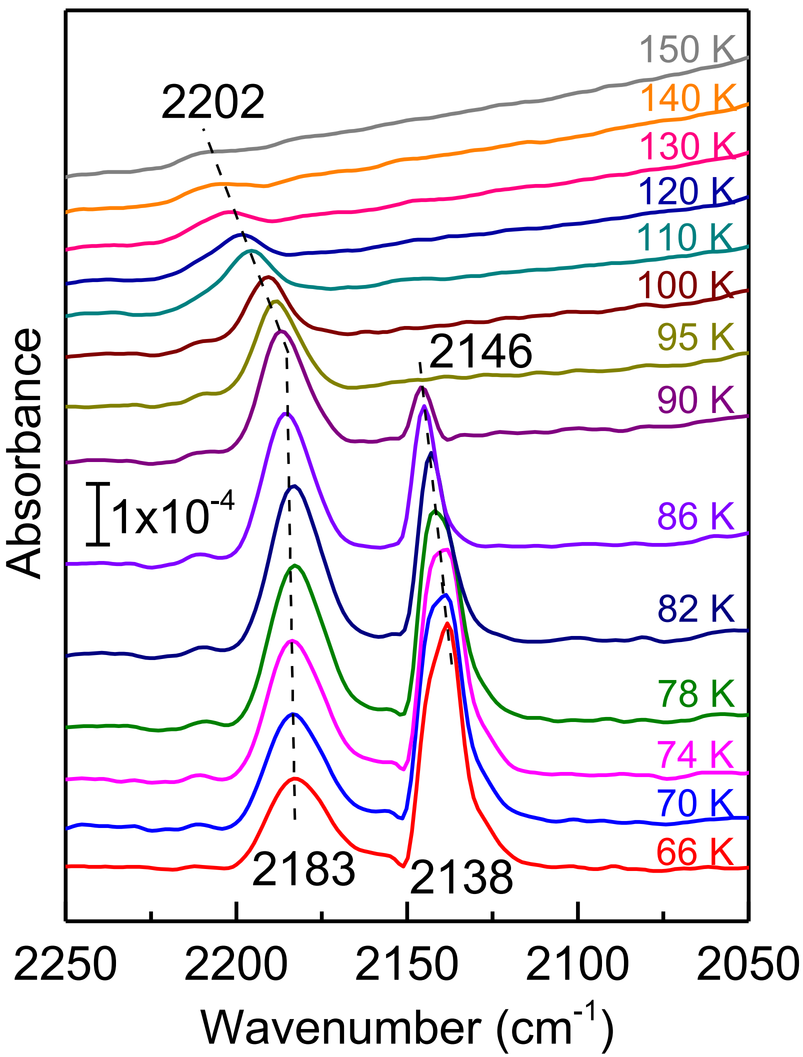
ZnO/Ag(111): growth of ZnO thin films monitored by IRRAS

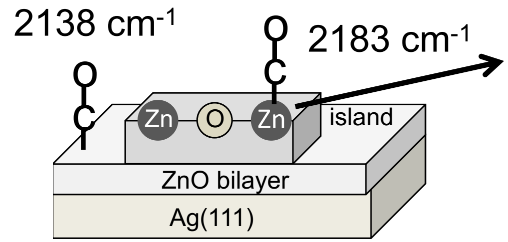


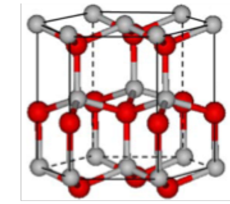


M. Andersen, X. Yu, et al., *J. Phys. Chem. C* 122 (2018), 4963−4971.

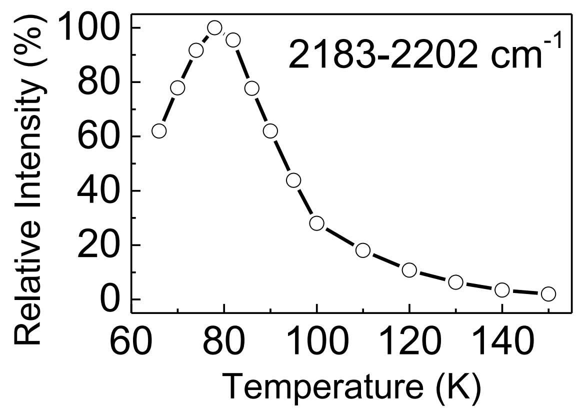
ZnO/Ag(111): Temperature-dependent IRRAS data



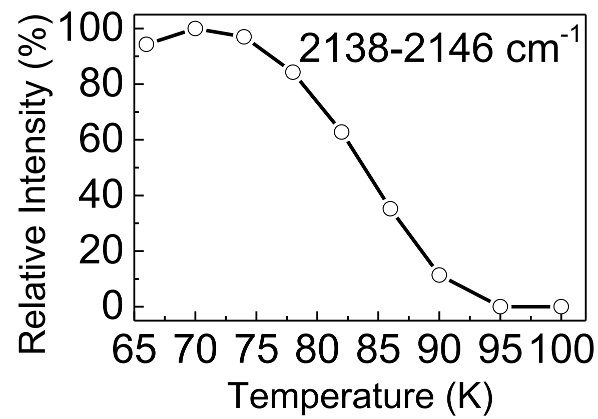




Wurtzite ZnO



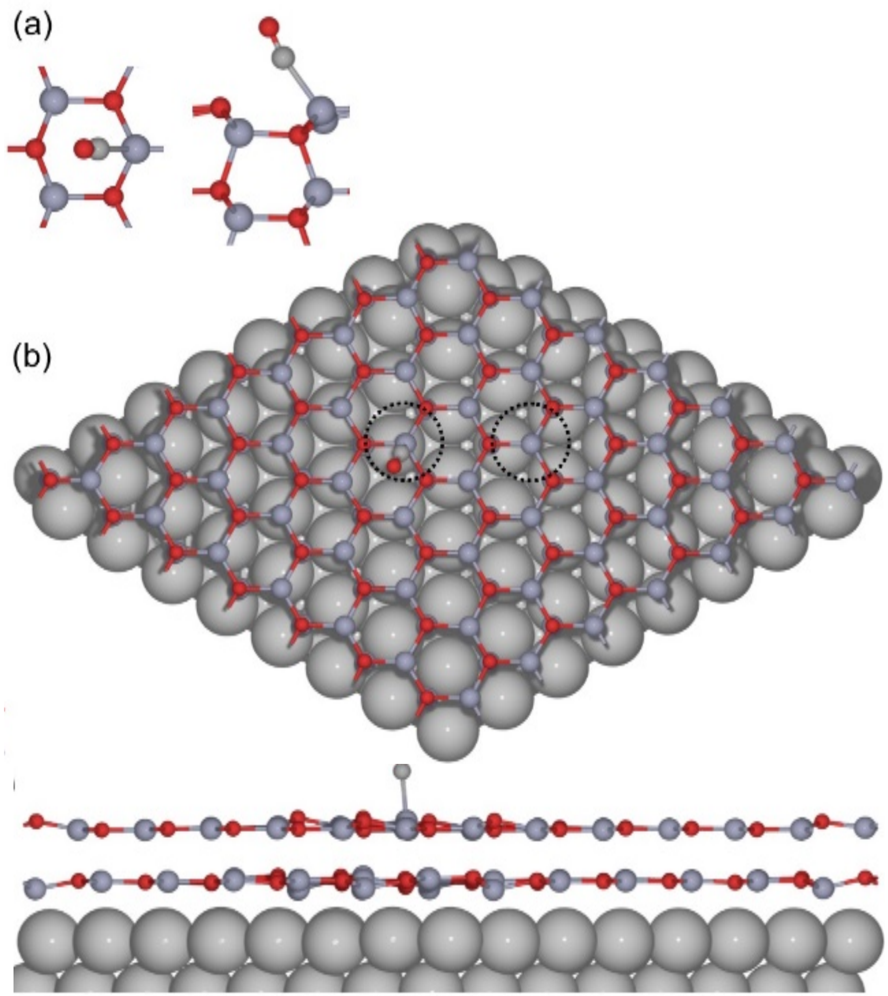
BE: 0.30 eV (29 kJ/mol)



BE: 0.24 eV (23 kJ/mol)

M. Andersen, X. Yu, et al., *J. Phys. Chem. C* 122 (2018), 4963−4971.

ZnO/Ag(111): growth of ZnO thin films calculated by DFT



System	Method	E_{CO} (eV)	$\Delta\nu_{CO}$ (cm^{-1})
ZnO$(10\bar{1}0)$	DFT	0.47	+37
	Exp.	0.32[1]	+42[1]
(7×7)ZnO/ (8×8)Ag	DFT: Site I	0.36	+5
	DFT: Site II	0.24	−3
	Exp.	0.24	+3

[1] Y. Wang, C. Wöll, Chem. Soc. Rev., 2017, 46, 1875.

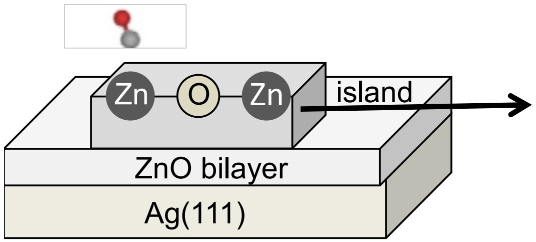
E_{CO}: CO adsorption energies

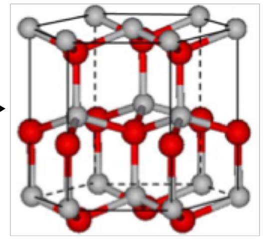
$\Delta\nu_{CO}$: shift of the CO vibrational frequency with respect to the gas phase value

DFT-optimized structures (top and side view) of CO adsorbed on (a) the wurtzite $(10\bar{1}0)$ surface, (b) the large (7×7)ZnO/(8×8)Ag structure. In (b) the dashed black circles highlight adsorption site I (shown structure) and II (empty circle).

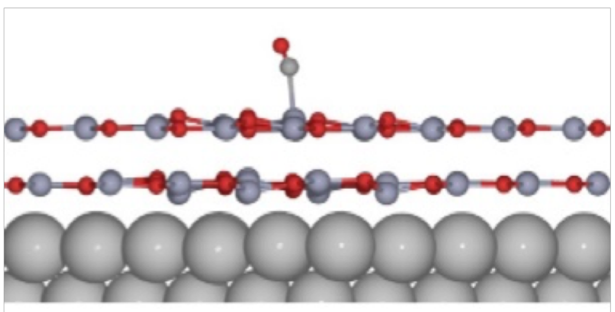
M. Andersen, X. Yu, et al., *J. Phys. Chem. C* 122 (2018), 4963−4971.

Comparison: different ZnO thin films monitored by IRRAS



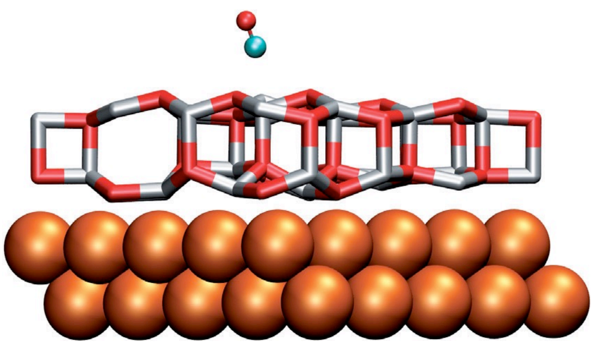


Wurtzite ZnO



Graphitic ZnO

Ag



Corrugated ZnO

Cu

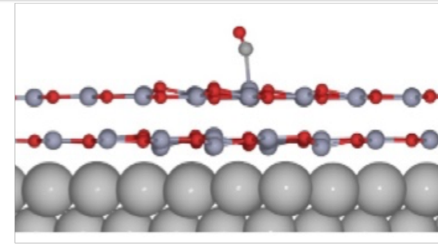
- CO on wurtzite-type ZnO islands (2183-2202 cm^{-1})
  Binding energy : 0.30 eV (29 kJ/mol)
  - CO on ZnO$(10\bar{1}0)$
    BE : 0.32 eV [1]
  - CO on ZnO(0001)
    BE : 0.28 eV [1]

- CO on graphitic-like ZnO bilayer (2138-2146 cm^{-1})
  Binding energy : 0.24 eV (23 kJ/mol)

- CO on ZnO/Cu(111) : corrugated bilayer
  2116 cm^{-1}, BE : 0.54 eV [2]

[1] Y. Wang, C. Wöll, Chem. Soc. Rev., 2017, 46, 1875.
[2] V. Schott, et al., Angew. Chemie, Int. Ed. 2013, 52, 11925

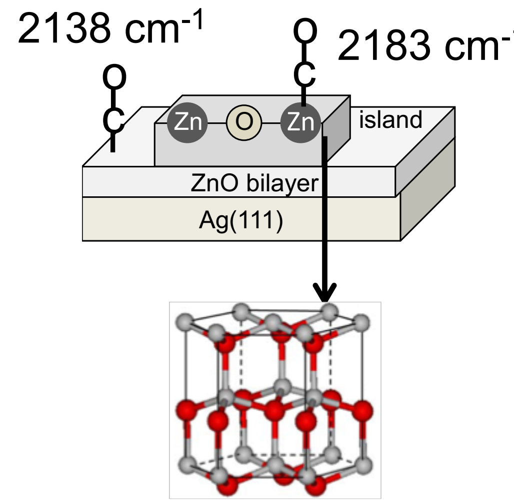
Conclusions



- Metal support plays a crucial role in the chemical activity of ZnO thin layers.
- **CO on ZnO/Ag(111) (<2 ML, graphitic bilayer)**

  ν(C-O): 2146 cm^{-1}; BE: 0.24 eV
- **Weak interaction between ZnO thin layers and Ag substrate**
- **CO on ZnO/Ag(111) (3-4 ML, wurtzite-like islands)**

  ν(C-O): 2183 cm^{-1}; BE: 0.30 eV



Acknowledgements

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Thank you for your attention!