Karlsruhe Institute of Technology

Structure of ultra-thin ZnO films supported on Zn/Ag alloy characterized by XPS/IR spectroscopy

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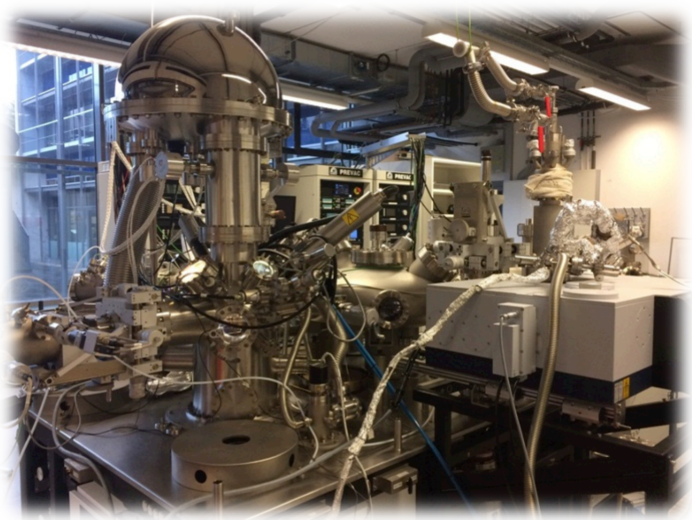
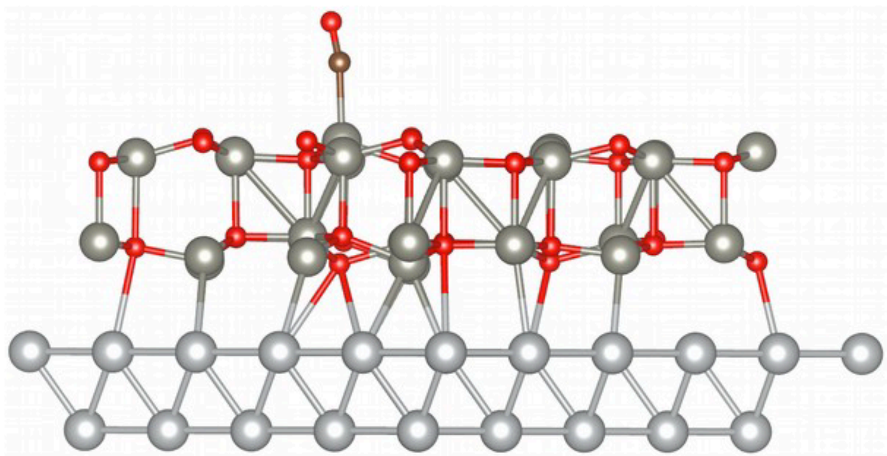
Institute of Functional Interfaces, Chemistry of oxydic and organic Interfaces





Introduction

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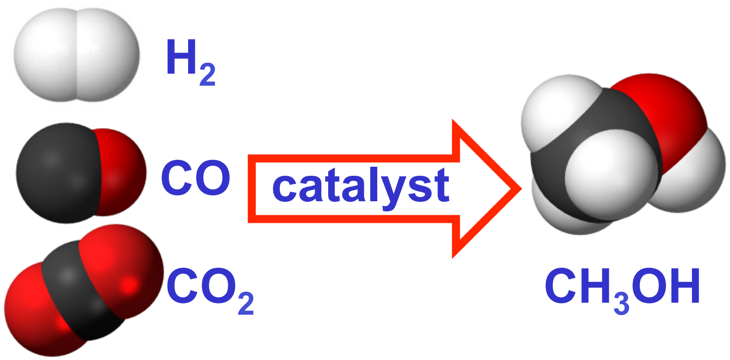
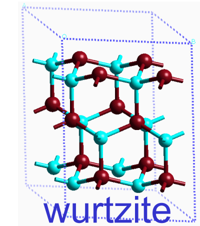
Catalyst : $Cu/ZnO/Al_2O_3$

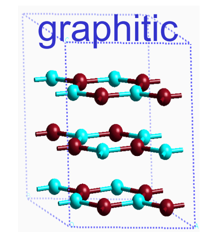


Catalyst : $Cu/ZnO/Al_2O_3$

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

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



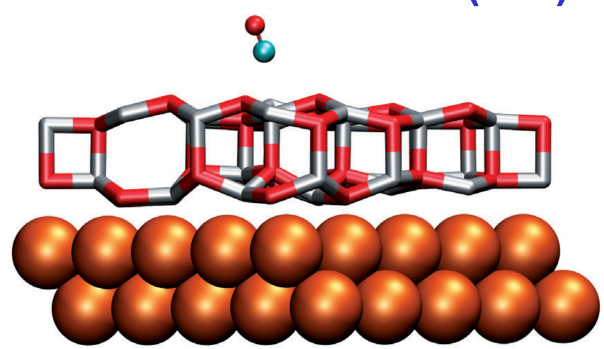


ZnO thin films

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

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

IRRAS:ZnO/brass(111)

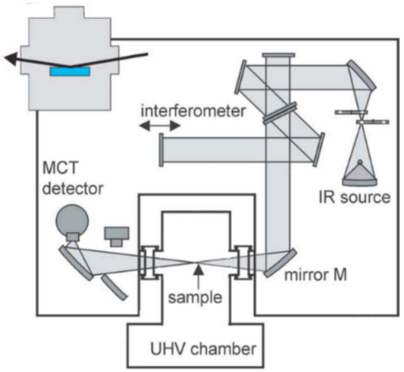


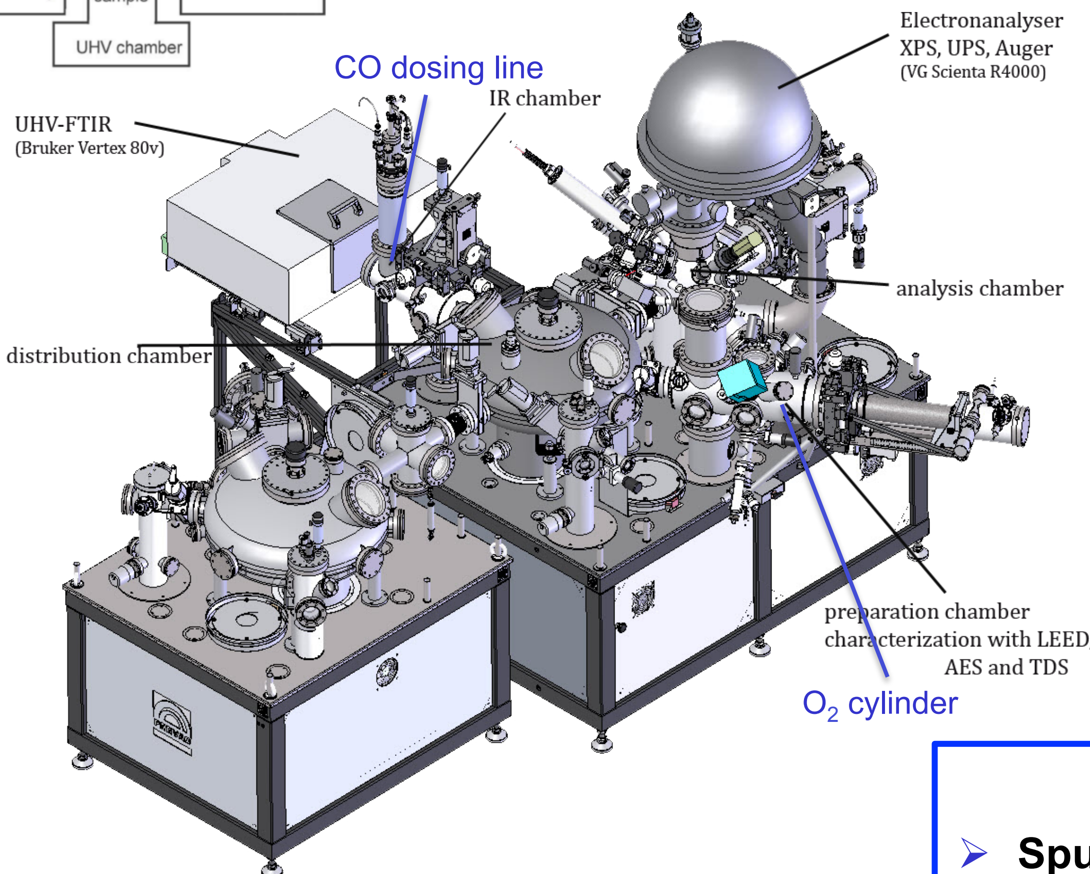
V. Schott et al., Angew. Chem. Int. Ed. **2013**, 52, 11925.

IRRAS : ZnO on Zn/Ag alloy

ZnO thin films
Zn/Ag alloy single crystal

Experimental





IRRAS-Measurements

- **Pressure: < 1×10^{-10} mbar**
- **Reflection mode**
- **Grazing Incidence (80°)**
- **T_{sample}: down to 55 K (LHe)**

Experiments

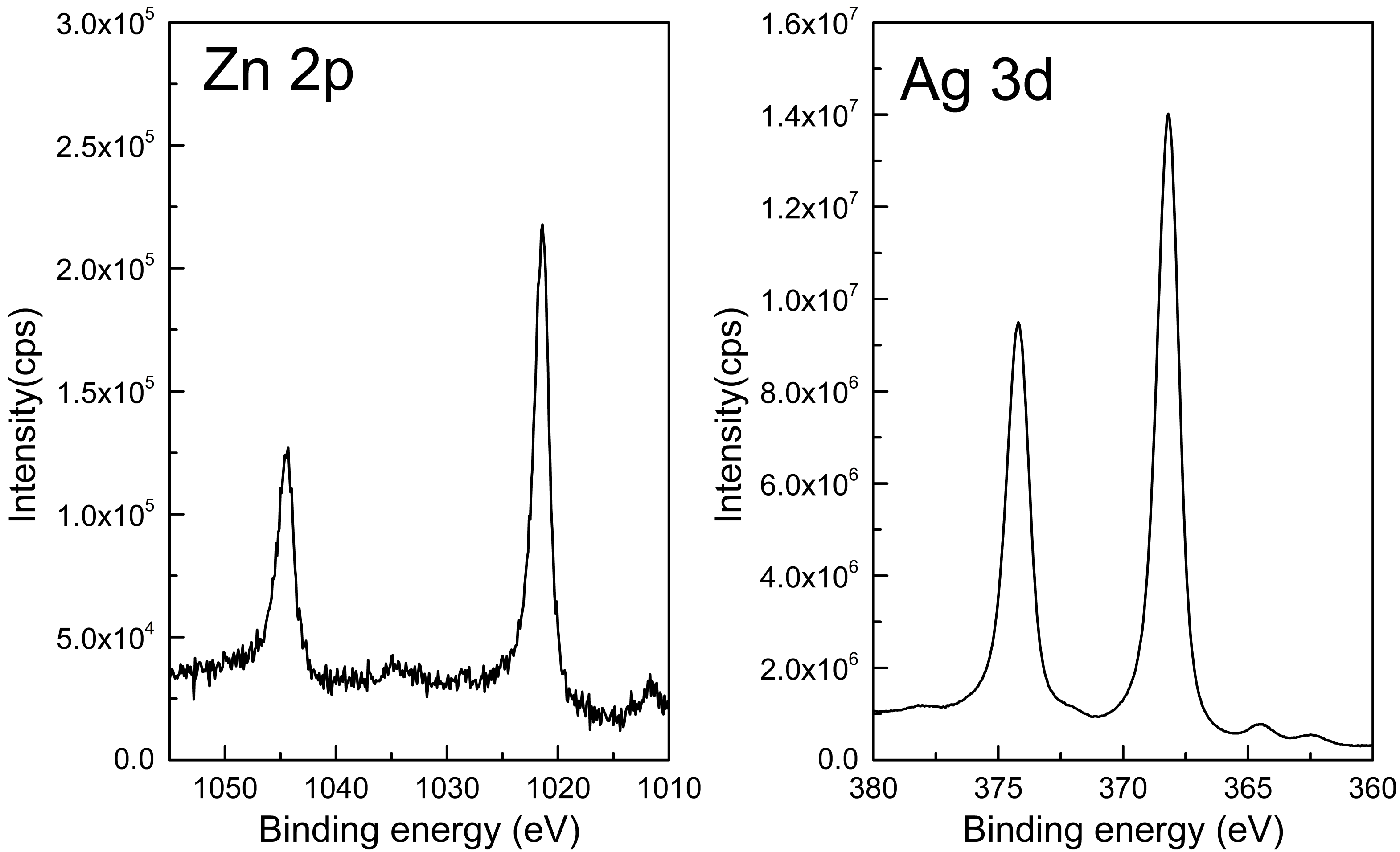
- **XPS : oxidation procedures**
- **IRRAS : CO adsorption**

Sample Preparation

- **Sputter-Anneal-Cycles**
- **XPS: sample cleanliness/oxidation**

Results

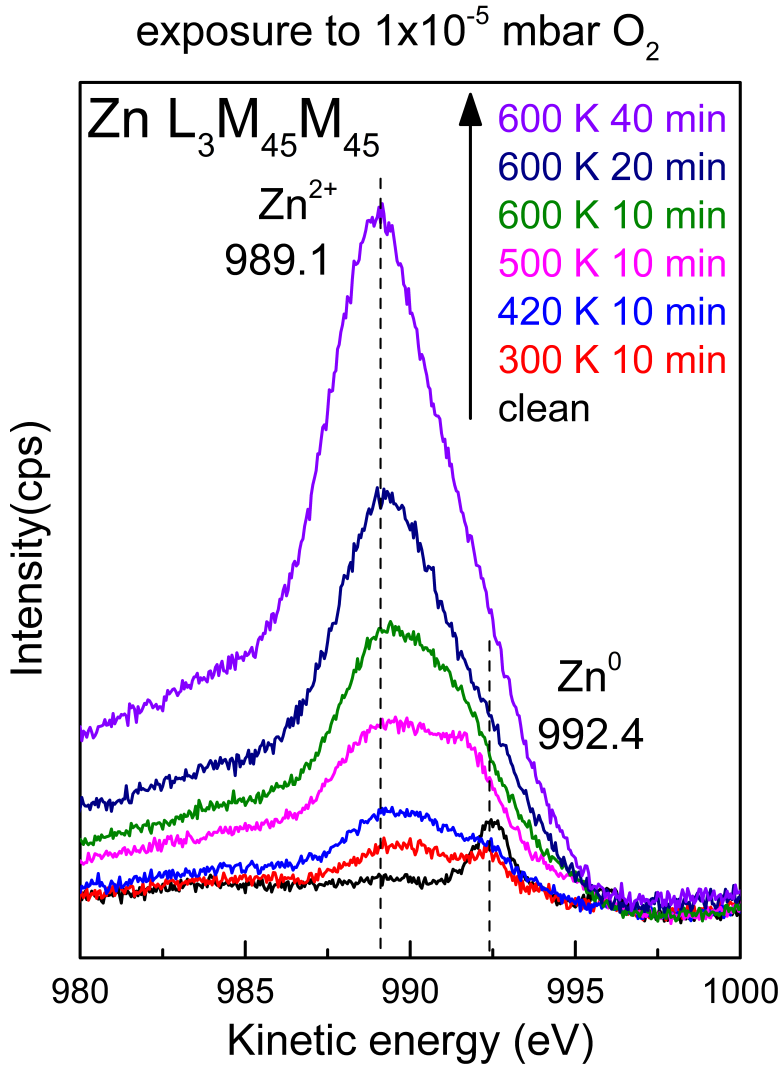
XPS data of Zn/Ag alloy: clean surface

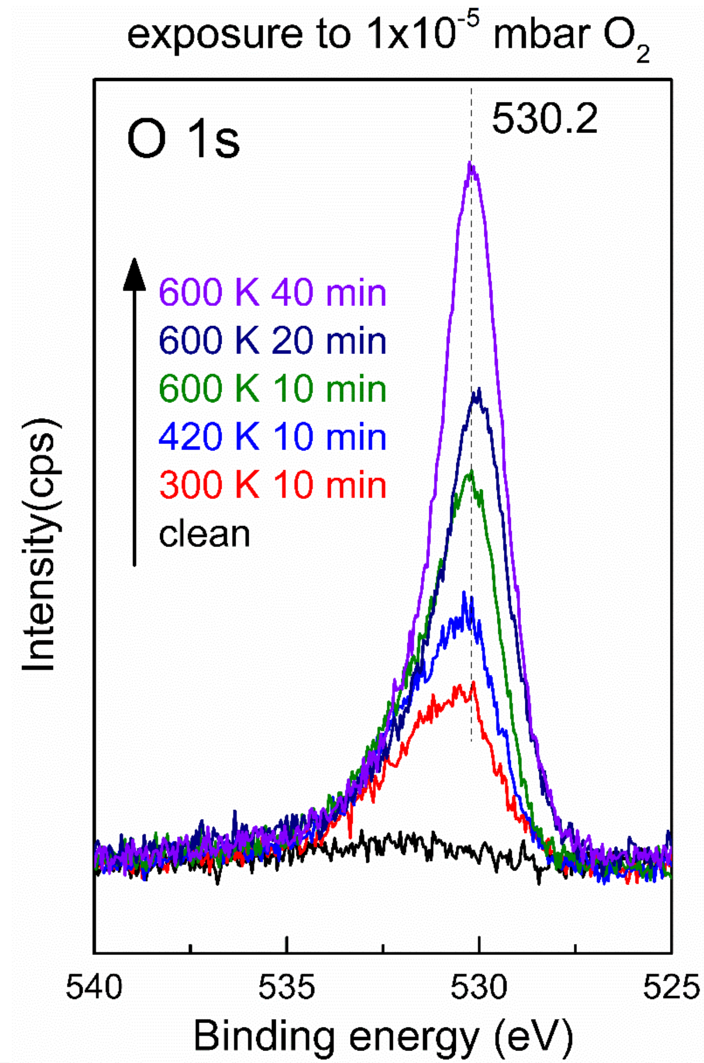


For the clean alloy surface, the concentration of Zn atom is lower than 2 % .

Results

Grazing XPS data : different oxidation procedures

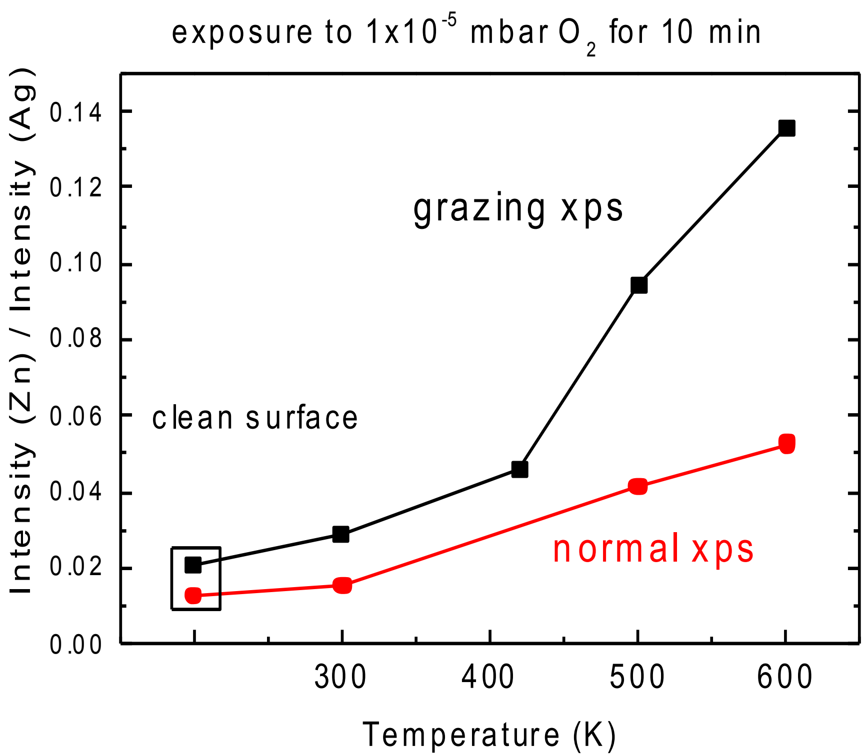




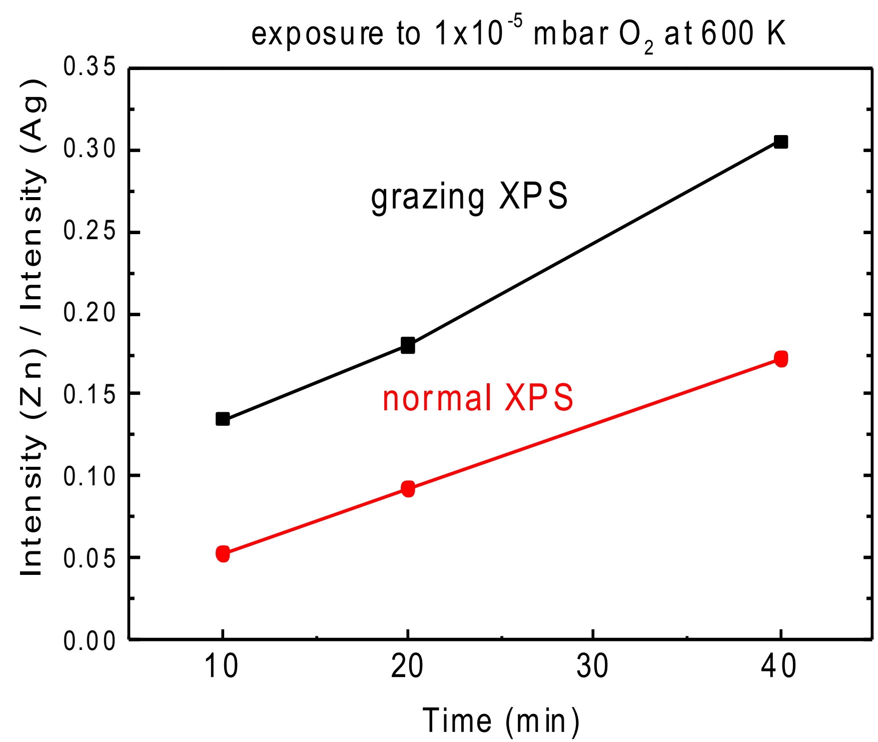
Results

Growth of ZnO thin layers on the surface

Temperature



Time



Results

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Thickness of the thin ZnO layers

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

$T_{A/S}$: the detector efficiency at $E_{kin,k}$;

$I_{A/S}$: the intensities of the adsorbate (Zn) and substrate (Ag) signal;

$\sigma_{\frac{A}{S}}$: the photoionization cross-section;

$n_{\frac{A}{B}}$: the atomic density of the analyzed species;

$\lambda_A(E_A), \lambda_S(E_S)$ and $\lambda_A(E_S)$: the mean free paths of the photoelectrons.

Exposure to 40 min O_2 at 600 K

wurzite structure: 1.7 Å

graphitic structure: 2.1 Å

Exposure the sample to 1×10^{-5} mbar of O_2 at 600K for 40 min:

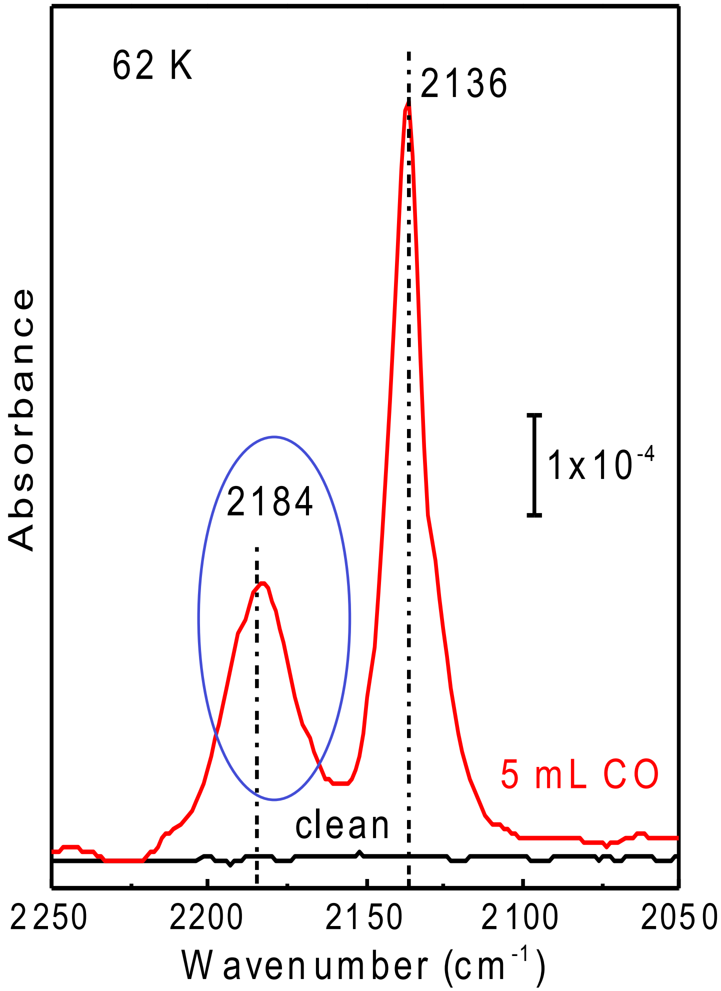
$I_{Zn2p\ 3\backslash2} = 1.84\times10^{6}$	$I_{Ag3d\ 5\backslash2} = 1.11\times10^{7}$
$\sigma_{Zn2p\ 3\backslash2} = 18.92$ [2]	$\sigma_{Ag3d\ 5\backslash2} = 10.66$ [2]
$n_{ZnO} = 4.89\times10^{-2}$ atoms/Å^3 (wurzite) [3,4] $n_{ZnO} = 4.08\times10^{-2}$ atoms/Å^3 (graphitic) [3,4]	$n_{Ag} = 5.89\times10^{-2}$ atoms/Å^3
λ_{Zn}(Zn 2p 3/2) = 11.96 Å [5] λ_{Zn}(Ag 3d 5/2) = 27.28 Å [5]	λ_{Ag}(Ag 3d 5/2) = 15.2 Å [6]

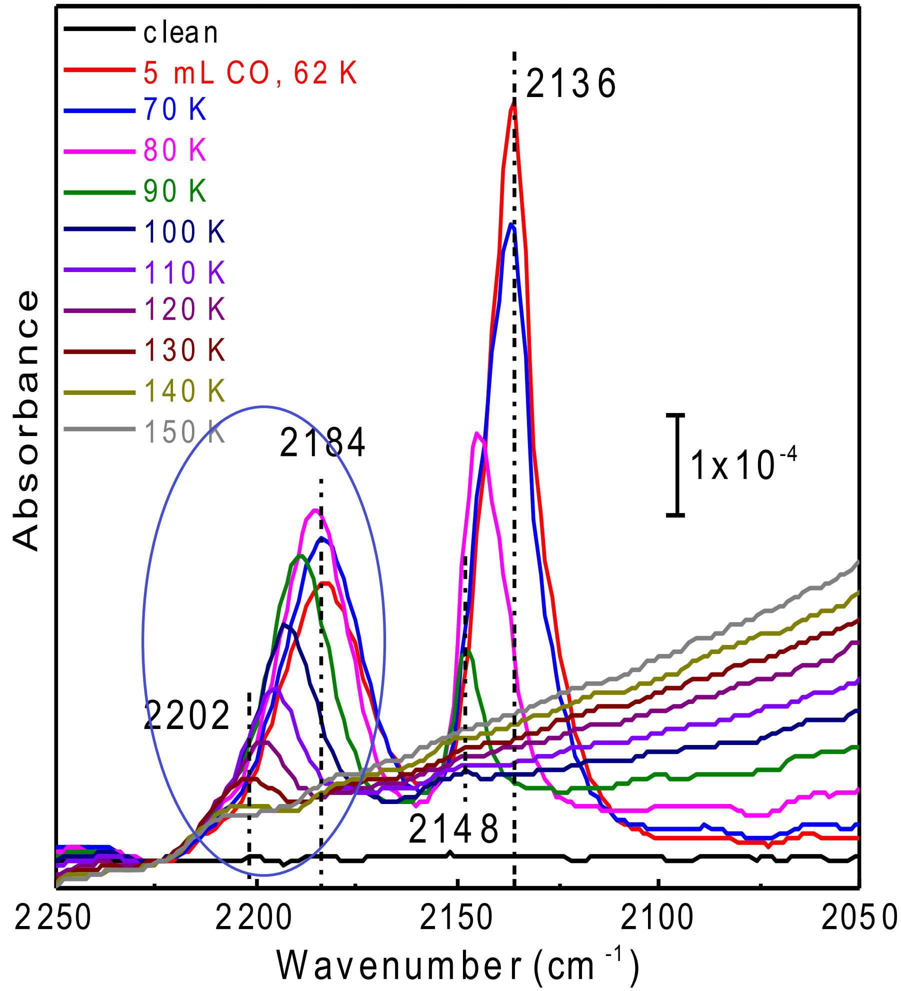
thin film: bilayer

[1] S. V. Merzlinkin et al., Surf. Sci. 602, 755-767 (2008). [2] J. H. Scofield, J. Electron. Spectrosc. Relat. Phenom. 8, 129-137 (1976).
[3] F. Claeyssens et al., J. Mater. Chem. 15, 139-148 (2005).[4] C. L. Freeman et al., Phys. Rev. Lett. 96, 066102 (2006).
[5] A. Akkerman et al., Physica Status Solidi B-Basic Research. 198, 769-784 (1996).[6] S. Tanuma et al., Surf. Interface Anal. 11, 577-589 (1988).

Results

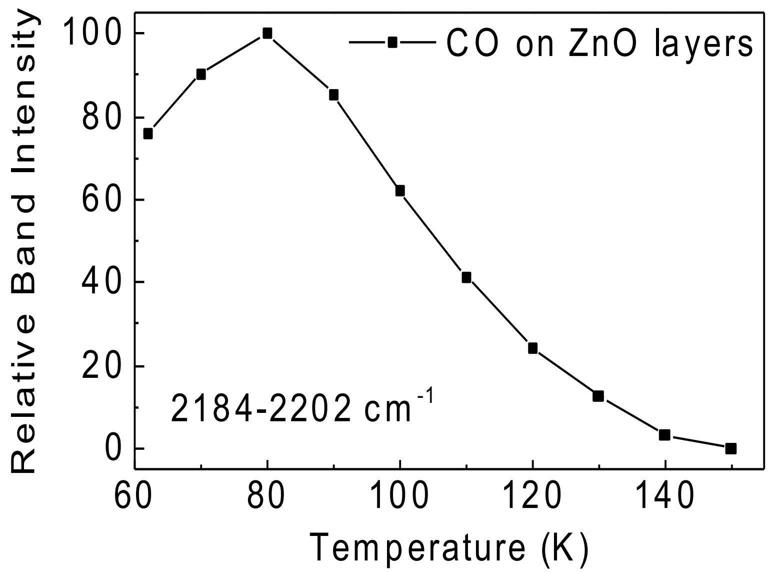
IRRAS data of CO adsorption on ZnO layers





Results

IRRAS thermal desorption data



BE = 0.33 eV (31.9 kJ/mol):
CO on ZnO layers

2143 cm^{-1} : gas phase CO

2170-2192 cm^{-1}: CO on ZnO(10-10)
2169-2192 cm^{-1}: CO on ZnO(11-20)
2178 cm^{-1}: CO on Zn-ZnO(0001)

2184-2202 cm^{-1}: CO on ZnO layers

Binding energy (BE):

0.32 eV: CO on ZnO(10-10)
0.28 eV: CO on Zn-ZnO(0001)
0.18 eV: CO on O-ZnO(000-1)

0.33 eV: CO on ZnO layers

Y. Wang et al., Angew. Chem. 46, 7315 (2007)
M. Buchholz et al., Surf. Sci. 652, 247-252 (2016)
C. Wöll, Prog. Surf. Sci. 82, 55-120 (2007)
V. Schott et al., Angew. Chem. Int. Ed. 52, 11925 (2013)

CO adsorbs weakly at Zn^{2+}

Structure of ZnO thin layers on Zn/Ag alloy

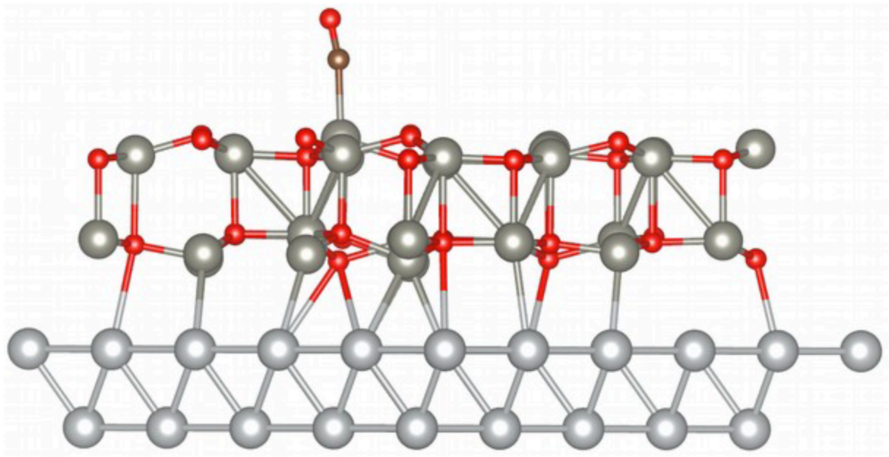
IRRAS results

2184 - 2202 cm^{-1} : CO on ZnO layers

Binding energy : 0.33 eV (31.9 kJ/mol)

2143 cm^{-1} : gas phase CO

CO on ZnO/Ag(111)



color code: oxygen = red, zinc = dark gray, silver = lignt gray

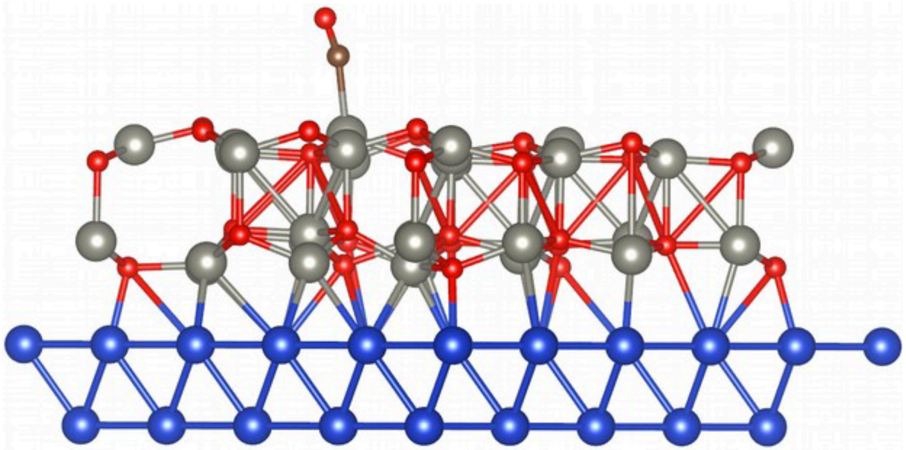
DFT calculations: blue shift

I. Demiroglu et. al, J. Phys. Condens. Matter 28, 224007 (2016)

Results

Structure of ZnO thin layers on Zn/Ag alloy

CO on ZnO/Cu(111)



color code: oxygen = red, zinc = dark gray, copper = blue

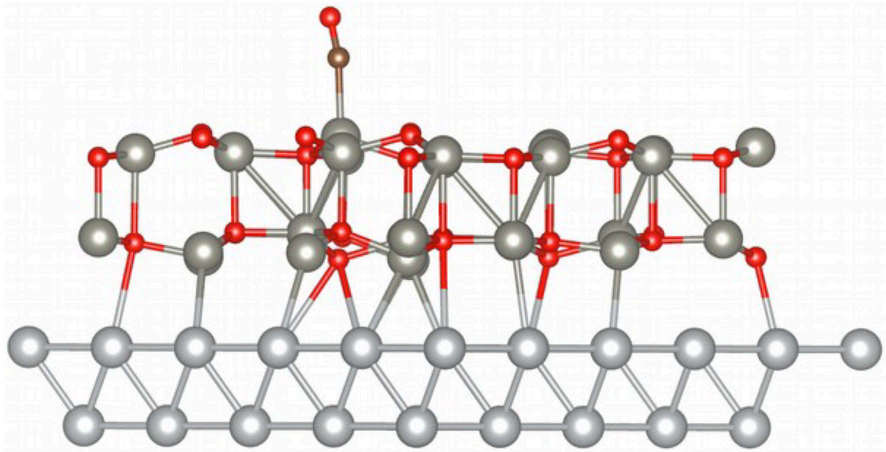
DFT calculations: red shift

2116 cm^{-1}, BE = 0.54 eV

V. Schott et al., Angew. Chem. Int. Ed. 52, 11925 (2013)

Strong interaction between ZnO and Cu substrate

CO on ZnO/Ag(111)



color code: oxygen = red, zinc = dark gray, silver = lignt gray

DFT calculations: blue shift

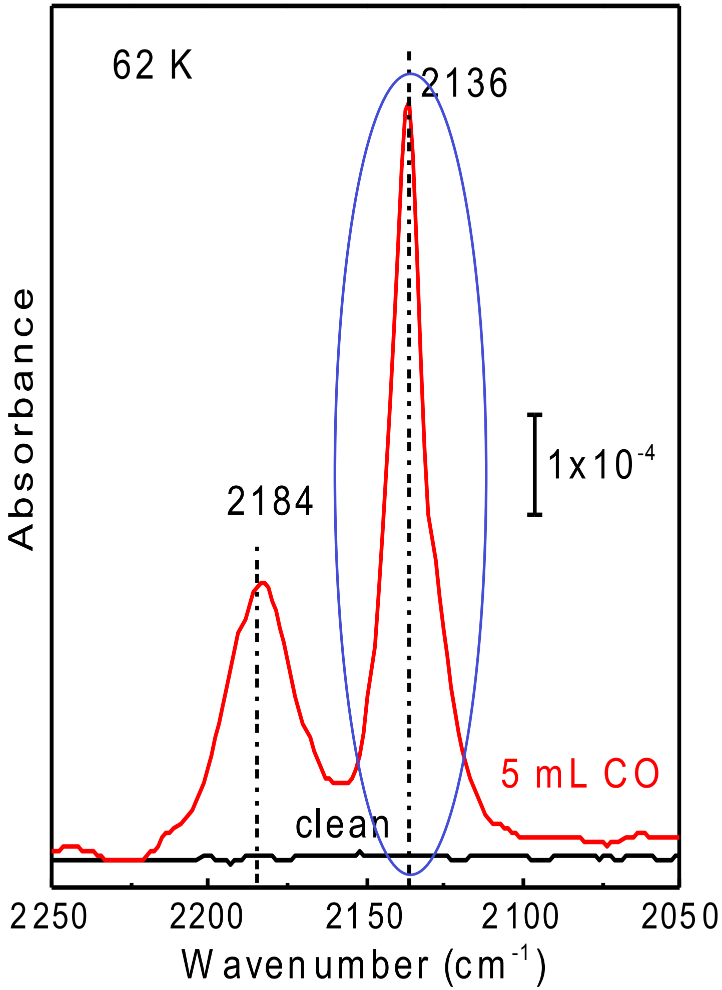
I. Demiroglu et. al, J. Phys. Condens. Matter 28, 224007 (2016)

2184-2202 cm^{-1}, BE = 0.33 eV

Weak interaction between ZnO and Ag substrate

Results

IRRAS data of CO adsorption on ZnO layers



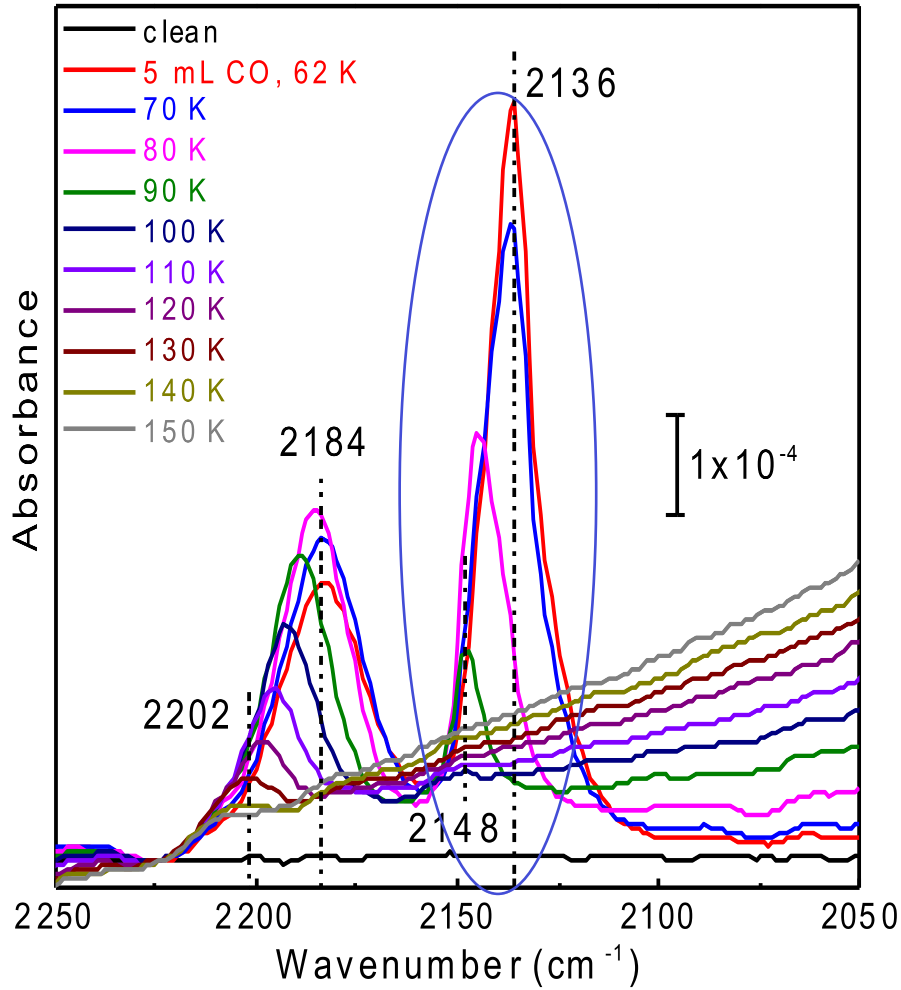
2136 cm^{-1} ?

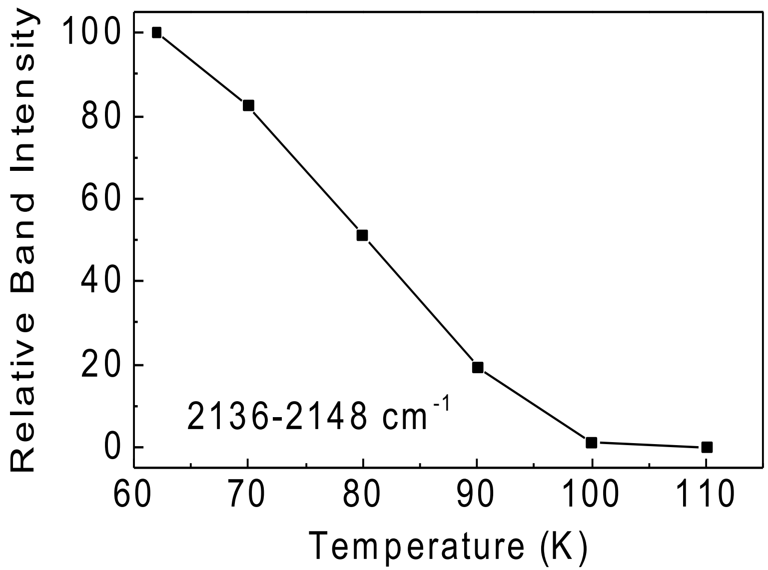
CO is only physisorbed on Ag(111) at surface temperatures below 48 K

K. Jacobi et al., Surf. Sci. 253, 1-12 (1991)
L. Fleck et al., J. Chem. Phys. 106 , 3813 (1997)

Results

IRRAS data of CO adsorption on ZnO layers





Binding Energy : 0.24 eV (23 kJ/mol)

Complete desorption at 100 K.

CO weakly bound to surface OH groups ?

Conclusions

➢ Exposure the Zn/Ag alloy to $1x10^{-5}$ mbar of O_2 at 600 K for 40 min yields ZnO thin layers (**2.1 Å, bilayer)** .

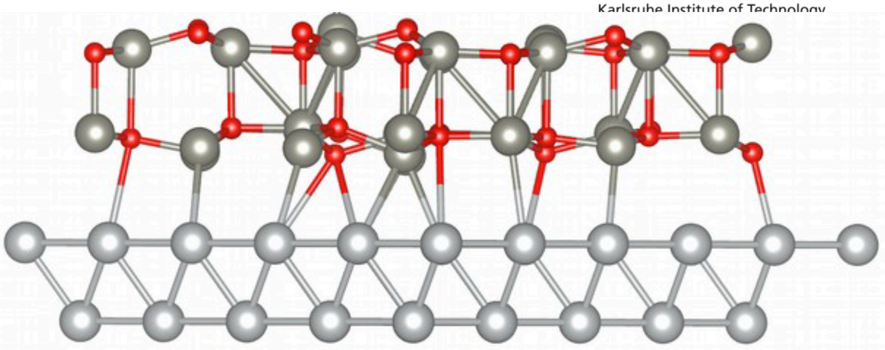
➢ ZnO thin layers adopt a distorted structure in between the ideal wurtzite and the planar graphitic structure.

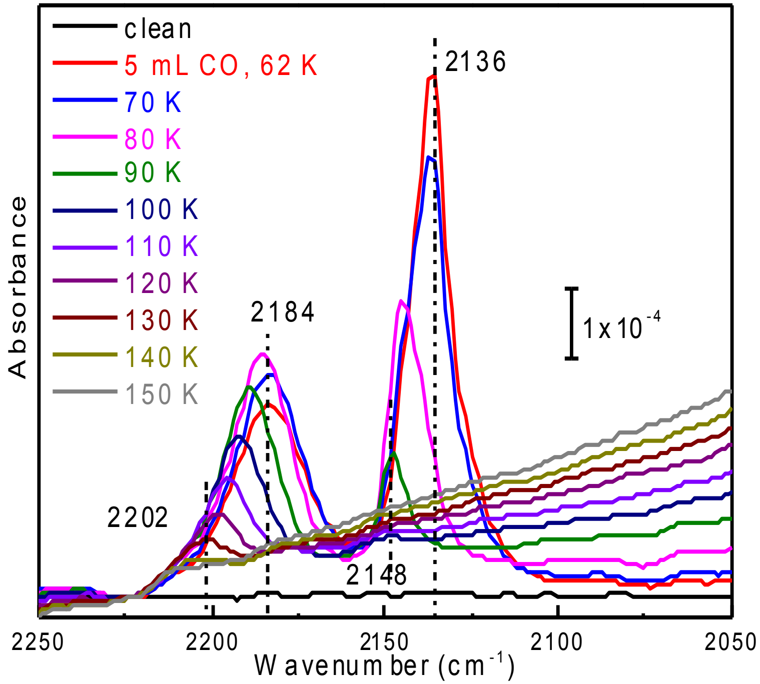
ν(C−O): 2184-2202 cm^{-1}

Binding energy: 0.33 eV (31.9 kJ/mol)

➢ CO adsorbs weakly at Zn^{2+}

➢ Weak interaction between ZnO thin layers and Ag substrate.





Thank you for your attention!