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Structural and chemical properties of ultrathin ZnO films supported on AgZn(111) surfaces

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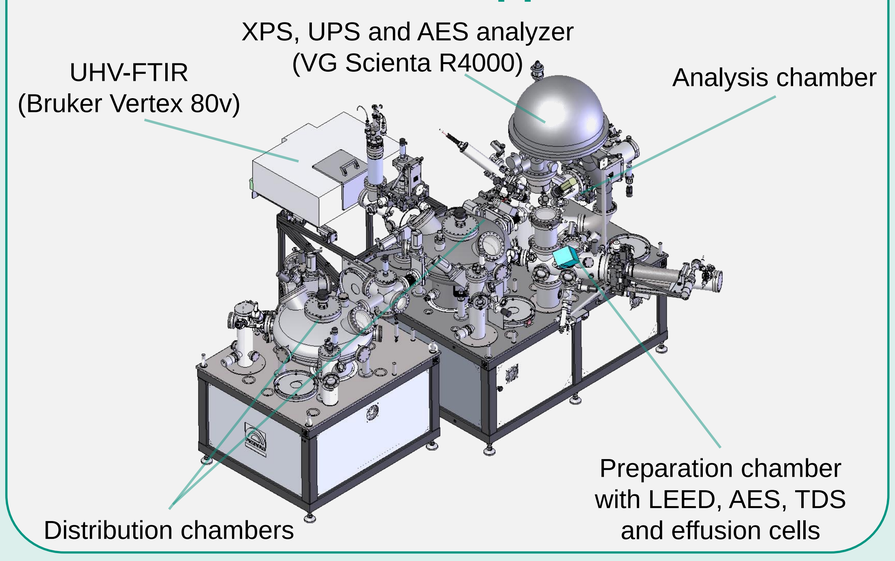
Introduction

The importance of ultrathin oxide films supported on metals under reaction conditions has been pointed out in many studies. The particular interest in ZnO films has recently been reinforced due to the observation of interlayer structural relaxations resulting in depolarized graphitic structures. Here, we report a thorough surface-science study on the structural and reactive properties of ultrathin ZnO adlayers formed on the AgZn(111) surface (Ag/Zn ratio 9:1) under different oxidation conditions. The evolution of ZnO thin films on AgZn(111) was monitored by X-ray photoelectron spectroscopy (XPS) and infrared reflection–absorption spectroscopy (IRRAS) using CO as a probe molecule [1]. The interaction of water with different types of ZnO adlayers was subsequently investigated.

UHV-IR/XPS apparatus



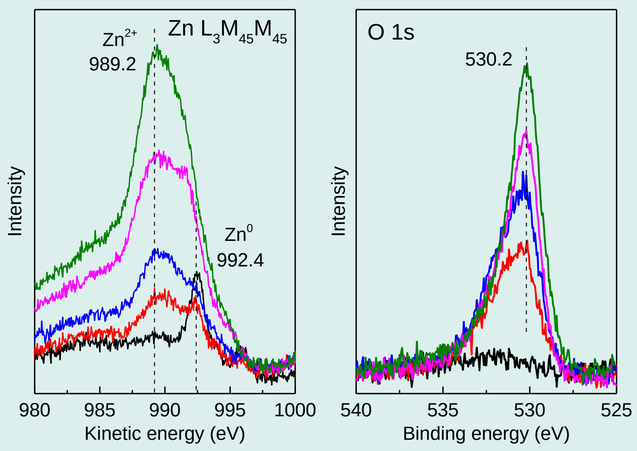
Experimental

The IRRAS and XPS measurements were performed in a state-of-the-art UHV-IR/XPS apparatus [2]. The AgZn(111) single-crystal surface (Ag/Zn ratio 9:1) was cleaned by cycles of Ar^+ sputtering at room temperature, followed by annealing at 420 K.

Exposure to CO at LHe temperature as well as water at LN_2 temperature was achieved by using a leak-valve-based directional doser connected to a tube.

The binding energy of CO adsorbed to different sites was estimated based on temperature-dependent IR experiments. IR spectra were recorded continually while heating the sample with a constant rate of 0.05 K/s. The normalized peak areas were shown as a function of temperature.

Surface analysis with grazing-emission XPS



- Why X-AES?

  The ZnLMM spectra are sensitive to the oxidation state of zinc (4 eV between Zn^{2+} and Zn^0)

- clean surface : black curve

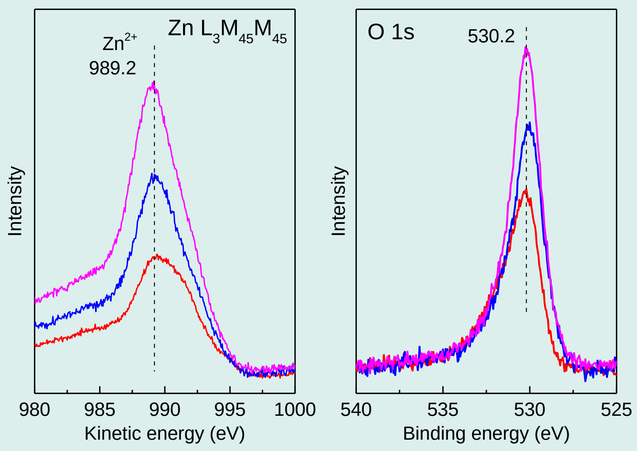
  main peak 992.4 eV (KE): metallic Zn^0

- oxidation with O_2 (1×10^{-5} mbar for 10 min)
  - red curve : 300 K

    typical Zn^{2+} $L_3M_{45}M_{45}$ peak : 989.2 eV

    O 1s (ZnO) : 530.2 eV
  - blue curve : 420 K
  - magenta curve : 500 K
  - olive curve : 600 K

- increase of the surface Zn concentration due to the formation of ZnO thin films



- oxidation with O_2 (1×10^{-5} mbar at 600 K)
  - red curve : 10 min

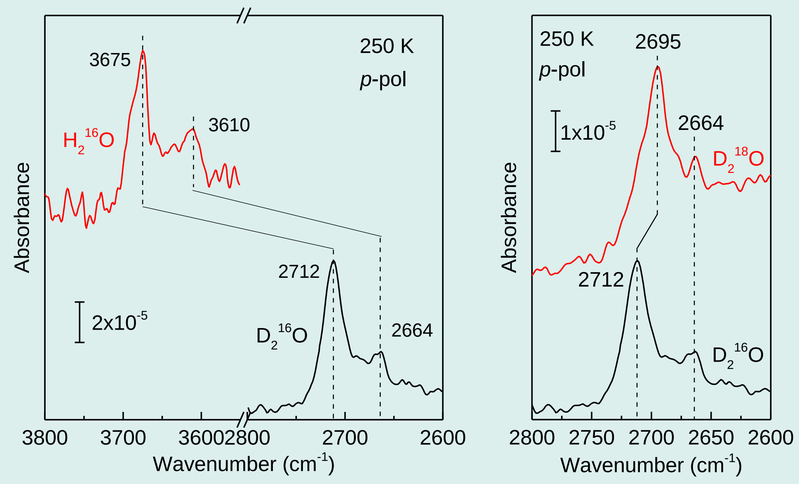
    1.9 Å (graphitic-type ZnO) : one monolayer
  - blue curve : 20 min

    3.4 Å (graphitic-type ZnO) : bilayer
  - magenta curve : 40 min

    4.4 Å (graphitic-type ZnO) : island

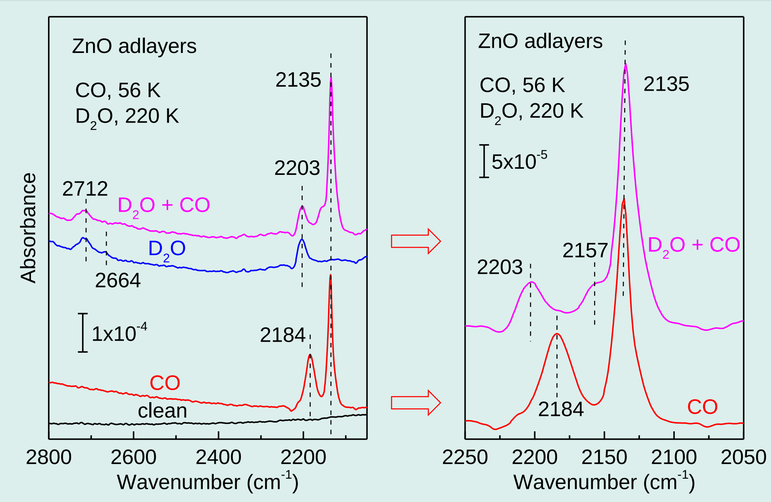
  or 3.7 Å (wurztite-type ZnO) : island
- increase of the surface Zn concentration due to the formation of ZnO thin films

Water adsorption on ZnO/Ag(111)



- The graphitic ZnO bilayer: moleular adsorption of D_2O
- The wurtzite ZnO island: full dissociation of D_2O
- 2664 cm^{-1}: ^{16}OD groups formed via hydrogen transfer to substrate ^{16}O
- 2712 / 2695 cm^{-1}: $^{16}OD/^{18}OD$ groups created by dissociation of $D_2{}^{16}O/D_2{}^{18}O$ molecules

CO and D_2O co-adsorption on ZnO/Ag(111)



- 2135 cm^{-1}:

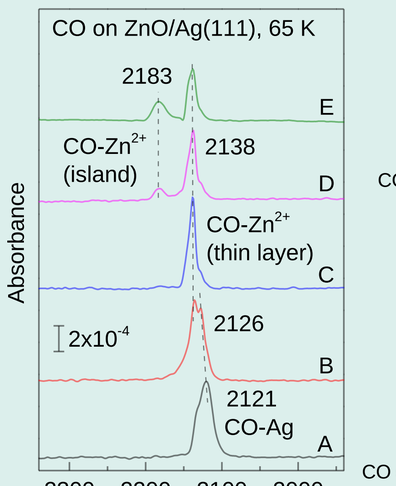
  CO on Zn^{2+} (bilayer)
- 2184 cm^{-1}:

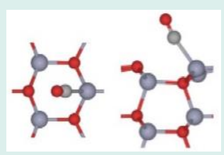
  CO on Zn^{2+} (island)
- 2157 cm^{-1}:

  CO on substrate OD groups
- 2203 cm^{-1}:

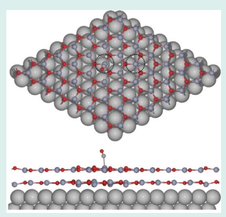
  Zn-O vibration

Structure evolution of ZnO films probed by CO adsorption





CO on wurtzite $(10\bar{1}0)$ surface [1]



CO on (7×7)ZnO/(8×8)Ag structure [1]

- E: oxidation with O_2 (600 K for 40 min)

  2183 cm^{-1} : CO on Zn^{2+} (island)
- D: oxidation with O_2 (600 K for 20 min)

  2138 cm^{-1} : CO on Zn^{2+} (bilayer)

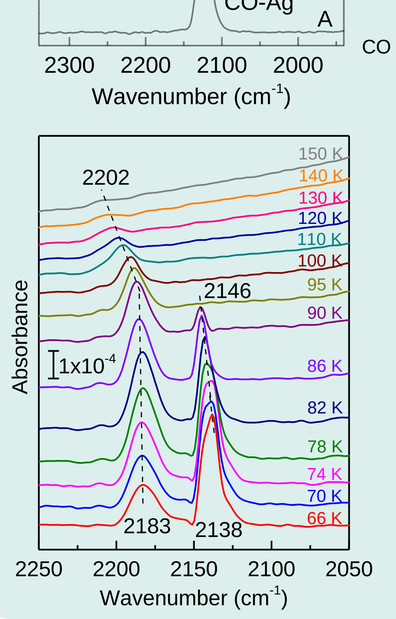
  2183 cm^{-1} : CO on Zn^{2+} (island)
- C: oxidation with O_2 (600 K for 10 min)

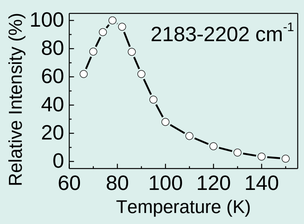
  2138 cm^{-1} : CO on Zn^{2+} (monolayer)
- B: oxidation with O_2 (500 K for 10 min)

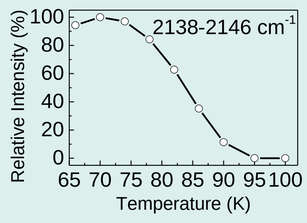
  2126 cm^{-1} : CO on Ag

  2136 cm^{-1} : CO on Zn^{2+} (submonolayer)
- A : clean surface

  2121 cm^{-1} : CO on Ag







- CO on wurtzite-type ZnO islands (2183-2202 cm^{-1})

  Binding energy : 0.30 eV (29 kJ/mol)
  - CO on $ZnO(10\bar{1}0)$

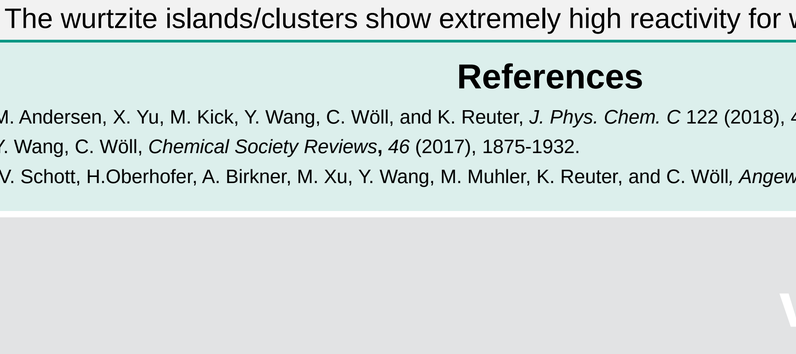
    BE : 0.32 eV [2]
  - CO on $ZnO(0001)$

    BE : 0.28 eV [2]
- CO on graphitic-like ZnO bilayer (2136-2146 cm^{-1})

  Binding energy : 0.24 eV (23 kJ/mol)

- ZnO/Cu(111) : corrugated bilayer

  2116 cm^{-1}, 0.54 eV [3]



- 2135-2147 cm^{-1}:

  CO on Zn^{2+} (bilayer)

  BE = 0.23 eV (21.8 kJ/mol)
- 2157 cm^{-1}:

  CO on substrate OD groups

  desorption temperature :

  around 75 K

Conclusions

- Metal support plays a crucial role in the structure and chemical activity of thin ZnO adlayers.
- The formation of a closed, graphitic-like ZnO bilayer on Ag(111) is characterized by a single sharp IR band at 2146 cm^{-1} for isolated CO molecules with a binding energy of 0.24 eV, indicating a rather weak interaction between CO and ZnO thin layers.
- The wurtzite-type ZnO islands are formed for coverage above 2 ML on Ag(111), the corresponding frequency at 2183 cm^{-1} and binding energy of 0.30 eV are consistent with those reported for CO adsorption on ZnO single-crystal surfaces.
- The wurtzite islands/clusters show extremely high reactivity for water dissociation.

References

[1] M. Andersen, X. Yu, M. Kick, Y. Wang, C. Wöll, and K. Reuter, *J. Phys. Chem. C* 122 (2018), 4963−4971.

[2] Y. Wang, C. Wöll, *Chemical Society Reviews*, *46* (2017), 1875-1932.

[3] V. Schott, H.Oberhofer, A. Birkner, M. Xu, Y. Wang, M. Muhler, K. Reuter, and C. Wöll, *Angew. Chem. Int. Ed.* 52 , 11925–11929 (2013).