

Influence of the Moiré Pattern on the Hydration of ZnO/Ag(111) and Cs Pre-Covered ZnO/Ag(111)

Dissertation

zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften (Dr. rer. nat.)

Lehrstuhl für Physikalische Chemie I der Fakultät für Chemie und Biochemie

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Bochum, Mai 2022

Abstract

This thesis is focusing on the interaction between water and ions on a Ag(111)supported ZnO ultrathin film. The structure of the ultrathin ZnO layers grown on a Ag(111) support is investigated by STM. The atomically flat ZnO are graphitic with a moiré pattern from the lattice. The adsorption and distribution of water are found to have the inhomogeneous distributions along the border and across the island is deduced to be the upward mass transport from metal to catalytically active metal-oxide border and the inward mass transport from the island border to more interior of the island for further reactions. Water nucleate on the hcp regions of the ZnO moiré pattern with a basic structure of hexamer. The presence of the Cs ion alters a bit the preference of water adsorption, forcing water molecules to adsorb partly near the Cs ion, forming hydrating Cs ion. The hydrated Cs ion connect with the existing water clusters, forming one-dimensional chain, thus, possibly influence its reactivity.

Kurzusammenfassung

Diese Arbeit befasst sich mit der Interaktion zwischen Wasser und Cs-Ionen auf einer ulltradünnen ZnO-Schicht auf Ag(111), untersucht mit Hilfe von STM. Das ZnO ist graphitisch und zeigt einen Moiré -Effekt. Die Adsorption führt zu einer inhomogenen Verteilung des Wassers an der Inselrändern und über die Inseln selber. Grund dafür ist ein Massetransport vom Metall hin zu der katalytisch aktiven Metall/Metalloxid-Grenze und, in einem weiteren Schritt, einem Massetransport von den Inselrändern hin zum Zentrum der Inseln. Das Wasserwachstum beginnt auf den hcp-Regionen des ZnO Moiré-Musters mit der Bildung eines Hexamers. Die Anwesenheit von Cs-Ionen ändert die bevorzugte Art der Wasseradsoption, indem es die Wassermoleküle zwingt nahe dem Ionen zu adsobieren und diese zu hydratisieren. Die hydratisierten Ionen verbinden sich mit den existierenden Wasserclustern, wobei sie 1-dimensionale Ketten ausbilden und so, möglicherweise, die Reaktivität positive beeinflussen.

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1 Introduction

With the development of industrial processes that required hydrogen, such as the ammonia synthesis process from Haber-Bosch, the production of pure hydrogen turns to people's eyes. The most important industrial method for the production of hydrogen is the steam reforming or steam methane reforming process (SMR). SMR is a method for producing synthesis gas, i.e., hydrogen and carbon monoxide, by reaction of hydrocarbon with water. The reaction equation is followed as:

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2$$
 (1)

The most widely used source of hydrocarbon is natural gas. However, due to the crisis of global warming and the drain of fossil fuels, people are searching for an alternative to not using hydrocarbons as a source to produce pure hydrogen for industrial needs. One of the industrial methods to produce pure hydrogen is the water gas shift reaction. The reaction equation is followed as:

$$CO + H_2O \longleftrightarrow CO_2 + H_2$$
 (2)

The reaction converts the carbon monoxide and water vapor to form carbon dioxide and hydrogen by using Cu/ZnO as a catalyst.

To understand the contribution of the different components in the catalysts, we concentrate on the ZnO. It is obvious that while studying the adsorption and reaction on an oxide surface, the oxide single crystal is the first choice. However, the poor electronic and thermal conductivity properties of the oxide disturb not only the sample cleaning under ultrahigh vacuum conditions but also prevent the use of electron-based spectroscopies and microscopies such as photoemission spectroscopy (PES), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM). As an alternative, forming an ultrathin oxide film on a metal support is a regularly utilized process. The ultrathin oxide films grown on metal single crystal supports, which also have a periodic structure, have been used as a model system to investigate the reaction mechanism in the heterogeneous catalyst at the atomic scale [1, 2]. The ultrathin film of ZnO was developed on several coinage metals such as Ag(111) [3,4], Au(111) [5], and Cu(111) [6]. To emphasize the contribution of the ultrathin ZnO film, the Ag(111) is used as metal support and investigates its structure and electronic configuration.

The interaction of water with surfaces is important in several scientific and industrial applications. Despite the importance of ultrathin oxide films for heterogeneous catalysis, very little is known about water growth and distribution on them. It is known that water

forms a 1D chain structure along the CaO < 110 > directions of a 20 ML CaO(001) film [7]. For an ultrathin iron oxide (FeO) film on Pt(111), water clusters form on hydroxylated and non-hydroxylated thin films [8]. In contrast to ultrathin FeO films, ultrathin films of ZnO supported on Ag(111) do not hydroxylate, not even upon exposure to molecular hydrogen or water [9]. Such ultrathin films are graphitic in contrast to thicker films [4] and thus different from bulk ZnO [10,11]. On a closed ZnO bilayer, grown via oxidation of AgZn(111), water adsorbs as an intact molecule [12]. Despite its importance for the water gas shift reaction, in particular at the catalytically active border between the oxide and the metal support, water structure and growth on an ultrathin film of ZnO and its border have not yet been addressed. Much more explored are the water structure and growth on metal surfaces [13]. Water coverages in the submonolayer regime lead to structures up to 4 ML in height on hydrophobic coin metals, on Cu(111) [14], Au(111) [15, 16], Ag(111) [17–19], and Ag(100) [20]. This suggests mass transport to higher layers during growth. For very low coverages, the most stable structure is a cyclic hexamer [21], which exists on Au(111) [16], Ag(111) [22], Cu(111) [21, 23], and on the ultrathin FeO film on Pt(111) [8]. Apart from hexamers, clusters of up to nine molecules form on the coinage metal surfaces [21] and up to 22 molecules on iron oxide [8]. We investigate the growth of water clusters on the graphitic ultrathin ZnO film with STM, discuss the influence of the moiré pattern on the nucleation of water clusters, and compare it with the structure of water clusters on Ag(111) and supported iron oxide. Furthermore, we investigate the reaction of the water on ZnO with PES and discuss the reaction mechanism with temperature.

The surface-doped alkali metals on the Cu/ZnO binary catalyst promote the water gas shift reaction in the order of Li < Na < K < Cs [24]. The reaction is promoted via suppressing the formation of the C–H bond by the presence of the surface alkali cations. It inhibits the synthesis of alcohols, by promoting the CO₂ desorption rather than its hydrogenation that produces alcohols [24,25]. Recent research has turned to a molecularscale understanding of the interaction of water with alkalis adsorbed on metal surfaces based on real-space imaging [26–29]. The first investigation in real-space on the hydration of the alkali cations were on the NaCl(001)/Au(111), suggesting that the diffusion rate of the ion hydrates depends on the degree of symmetry match between the ion hydrates and the surface lattice [26]. Lithium ions disperse water nanoislands on Au(111) and alters the water desorption kinetics [27]. These and other alkalis ionize upon adsorption on metallic surfaces, transferring almost a full electron to the metal [30–33]. A charge transfer also exists for metal-supported oxide surfaces, though to a smaller extent. While a Cs atom transfer nearly a full electron to the Cu(111) surface [28], to the Cu₂O/Cu(111) surface leading to a partially charged Cs^{δ +} ions [29]. This charge transfer is present on an O-terminated bulk ZnO(000 $\overline{1}$) surface, where Cs transfer partial charge to surface O atoms, forming a Cs^{δ +} ion [34]. However, neither the preferential adsorption region and the superstructure of the Cs^{δ +} ion on the ultrathin ZnO film nor its hydration have been addressed so far. We first investigate the structure of Cs adsorption on the moirépatterned ZnO, discuss the preferred adsorption regions, and further compare it with the preferred adsorption region of water clusters. Moreover, we compare the formation of the one-dimensional chain structures based on hydrating the Cs pre-covered and pristine moiré-patterned ZnO surface.

2 Theoretical Background

2.1 Growth

The following sections give a brief introduction to the process of nucleation and the growth modes of thin films.

2.1.1 Nucleation Process



Figure 1: Schematic diagram illustrating the hopping processes of diffusion.

The diffusion of the adatoms or the adsorbates on the surfaces affects the nucleation of adsorbates on the surface [35]. One of the common diffusion processes is thermal diffusion. The thermal diffusion process on the atomic scale is described as hopping diffusion. It describes how the adsorbate moves from one energetically preferable position to another one (Fig. 1). The one-dimensional mean free path of the hopping diffusion (Δx) is determined by the random walk:

$$<\Delta x^2>=\nu_{hopp}\cdot\Delta t\cdot d^2$$
 (3)

where ν_{hopp} is the hopping frequency, also known as the attempt frequency, Δt is the elapsed time, and the *d* is the mean jump length, which often refers to the lattice constant *a*. The mean free path of the hopping diffusion is also described by the Einstein relation:

$$<\Delta x^2 >= 2D\Delta t$$
 (4)

where the D is the diffusion coefficient or the diffusivity. Considering that the fcc(111) single crystal surfaces are considered isotropic, the mean free paths in the different directions of the surface are the same ($\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle = 2D\Delta t$). The transition state theory (TST) [36] of the adsorbate gives for diffusion an Arrhenius-like expression, which

depends on temperature:

$$D = D_0 exp(\frac{-E_{diff}}{k_B T}) \tag{5}$$

where E_{diff} is the activation energy of diffusion, k_B is the Boltzmann constant, T is the temperature, and D_0 is the prefactor of the diffusion coefficient. The prefactor diffusion coefficient is determined by:

$$D_0 = \frac{N_{ads}}{2N_{dim}} \cdot d^2 \cdot \nu_{hopp} exp(\frac{\Delta S_D}{k_B})$$
(6)

here the attempt frequency is around $\nu_{hopp} = 10^{12} - 10^{13}$ Hz, N_{ads} is the number of neighbouring equivalent adsorption sites, N_{dim} is the dimensionality of motion, and ΔS_D is the difference in entropy between the ground and transition state. For a quadratic surface, the $\frac{N_{ads}}{2N_{dim}}$ is equal to 1, and $\frac{N_{ads}}{2N_{dim}}$ is equal to 1.5 for a hexagonal surface.

2.1.2 Growth of Thin Films

Well-ordered thin films are prepared by evaporating the materials onto the surface. In this work, we are using the method of physical vapor deposition (PVD), which is based on the thermal evaporation of the material. Alternative deposition methods such as cathodic arc deposition [37], pulsed laser deposition [38], and sputter deposition [39] are also possible.



Figure 2: Illustration of the growth modes of thin films on surfaces: (a) layer-by-layer (Frank-van der Merwe, FM) growth mode, (b) island (Volmer-Weber, VW) growth mode, and (c) layer-plus-island (Stransky-Krastanov, SK) growth mode. (Modified from [40].)

The common processes of the thin film growth are in three different modes: layer-by-layer (Frank-van der Merwe, FM) growth, layer-plus-island (Stransky-Krastanov, SK) growth, and island (Volmer-Weber, VW) growth. In the layer-by-layer growth mode, the new layer grows only when the underneath layer is completely full (Fig. 2a), resulting in a two-dimensional growth mode. This effect comes from the deposited atoms being more attracted to the substrate than to each other.

For the island growth mode, the deposited atoms form three-dimensional islands before the first layer covers the substrate completely (Fig. 2b). It is because the interaction between deposited atoms is stronger than the interaction between overlayer and substrate.

The layer-plus-island growth mode is the intermediate mode between FM and VW (Fig. 2c). In this growth mode, the adsorbed atoms first grow in a layer-by-layer mode up to several monolayers (ML) thick on the substrate. Beyond this critical thickness, which depends on the strain and the chemical potential of the deposited film, the growth continues through forming three-dimensional islands. The strain is caused by the lattice mismatch between the thin film and the substrate.

2.2 Scanning Tunneling Microscopy

The scanning tunneling microscopy (STM) is a surface probe technique for imaging the electron density of conductive surfaces in a dimension of molecule or atomic scale in real space. It is based on the tunneling effect between the tip and sample with a specific tunneling bias V_t applied, resulting in a tunneling current I_t as a function of distance d:

$$I_t = k_1 \cdot V_t \cdot e^{-k_2 \cdot \sqrt{\phi} \cdot d} \tag{7}$$

where k_1 and k_2 are material constants and ϕ the tip-sample work function. Ideally, the apex of the tip should be a single atom.

In the constant current mode, which is used in this work, the current is kept at a certain set-point (I_t) . The feedback loop adjusts the tip height to maintain the corresponding tunneling current during the scan. A spatially resolved topographic map of local electron density is then generated from the control signal of the feedback loop.



Figure 3: Top: schematics of tunneling process between metallic tip and conducting sample. Middle: electrons of energies up to eV_t above the Fermi energy of the sample E_F^S may tunnel from occupied states (shaded) in the tip to unoccupied states in the sample (or vice versa, not shown). V_t is the applied bias that displaces the two Fermi levels of sample and tip against each other and eV_t is the energy difference between the Fermi levels. Bottom: the electron wave function ψ decays exponentially in the vacuum region between the two electrodes; d is the distance between the two electrodes. (Modified from [41].)

2.3 Photoemission Spectroscopy

Photoemission (electron) spectroscopy (PES) is a powerful spectroscopic method in surface science.



Figure 4: Photoemission process. $h\nu$: photon energy, E'_k : kinetic energy of the ejected electron, ϕ_s : work function of the sample, E_B : binding energy of the ejected electron, E_k : measured kinetic energy, E_p : pass energy, E_R : retarding field, ϕ_{sp} : work function of the analyzer, E_F : Fermi energy/level. (Modified from [42].)

A photon with energy $h\nu$ impacts an atom, the photon may interact with an orbital electron resulting in the electron emission with a total transfer of the photon energy (Fig. 4). The sample and spectrometer are grounded together, the Fermi level (E_F) of the sample and spectrometer are aligned and set to zero. If the electron receives energy enough to overcome the binding energy (E_B) and the work function of the sample (ϕ_s) , the electron is thus ejected with a kinetic energy (E'_k) . The relationship is given by:

$$E'_k = h\nu - E_B - \phi_s \tag{8}$$

where the kinetic energy depends on the work function of the sample (ϕ_s) , which is varied by the surface chemical environment. The ejected electrons pass through the lens system (Fig. 5) are then retarded by a retarding field (E_R) , determined by the lens voltages, before entering the analyzer (Fig. 5). The analyzer is a band pass filter which allows electrons with a kinetic energy very close to E_p to pass through and enter the detector. Therefore, the measured kinetic energy (E_k) of the electron follows a relationship between



Figure 5: Schematic view of the hemisphere analyzer (PHOIBOS 100, *SPECS*, with permission [43]).

the incident photon energy and the binding energy of the electrons (Fig. 4a and c):

$$E_{k} = E_{R} + E_{p} + \phi_{sp} = h\nu - E_{B}$$
(9)

which is independent of the sample work function (ϕ_s) . Note that the kinetic energy displayed by measurement devices is $(E_R + E_p)$, so that the binding energy reference to the Fermi level is calculated by:

$$E_B = h\nu - (E_R + E_p) - \phi_{sp}$$
 (10)

in which the work function of the spectrometer should be considered. A typical value for the work function of an analyzer (ϕ_{sp}) is between 4.2 eV to 4.8 eV [43]. It is included in the measurement software. Further calibration is done by PES spectra from known characteristic lines. For the experiments every x-ray photoemission spectrum is calibrated with the binding energy of Ag $3d_{5/2}$ of pristine Ag(111) at 368.3 eV [44].

2.4 Low Energy Electron Diffraction (LEED)

Low energy electron diffraction (LEED) is a surface science technique that is used to determine two-dimensional (2D) periodic structures or the long-range ordering of the surface structure. In the experiment, a monochromatic low energy (20–200 eV) electron beam is generated by a filament and is focused onto the surface (Fig. 6). The back-scattered electrons are filtered by grids to remove the inelastic electrons. These electrons are then further enhanced by a microchannel plate (MCP) producing a diffraction pattern that is visualized by a fluorescent screen. The electrons of this energy range have a de Broglie wavelength of around 0.1 nm, which makes LEED suitable for determining the inter atomic distances.



Figure 6: Schematic view of the MCP-LEED (modified from [45]).



Figure 7: An example of surface vector transformation: fcc(111).

Electrons scattered from a periodic crystal lattice are diffracted due to the wave nature of electrons. It is convenient to describe the diffraction in the reciprocal space. The relationship between real space (surface) lattice vectors and reciprocal lattice vectors is (Figure 7):

$$\begin{cases} \mathbf{a}_{1}^{*} = \frac{\mathbf{a}_{2} \times \mathbf{n}}{|\mathbf{a}_{1} \times \mathbf{a}_{2}|} \\ \mathbf{a}_{2}^{*} = \frac{\mathbf{a}_{1} \times \mathbf{n}}{|\mathbf{a}_{1} \times \mathbf{a}_{2}|} \\ \mathbf{a}_{1} \cdot \mathbf{a}_{2}^{*} = \mathbf{a}_{2} \cdot \mathbf{a}_{1}^{*} = 0 \end{cases}$$
(11)

where \mathbf{a}_1 and \mathbf{a}_2 are the real space surface lattice vectors, \mathbf{a}_1^* and \mathbf{a}_2^* are the reciprocal space vectors, and \mathbf{n} the unit vector with a direction of surface normal. For an incident electron beam with a wave vector of \mathbf{s}_0 and scattered wave vector \mathbf{s} , the condition of constructive interference and hence diffraction of scattered electron waves is given by the Laue condition (2D):

$$\mathbf{s}^{\parallel} - \mathbf{s}_{0}^{\parallel} = \mathbf{G}_{hk} = h\mathbf{a}_{1}^{*} + k\mathbf{a}_{2}^{*}$$
 (12)

where $\mathbf{s}_{0}^{||}$ and $\mathbf{s}^{||}$ are the components of the incident and scattered wave vector which are parallel to the surface plane, h and k are the Miller indices, and \mathbf{G}_{hk} is the reciprocal lattice vector. All solution of the Laue condition can be constructed as a sphere, so-called Ewald sphere (Fig. 8). The crossing points of the reciprocal lattice rods and the Ewald sphere result in the diffraction patterns.



Figure 8: The Ewald construction, dashed lines: the reciprocal lattice rods.

3 Experimental Setup

3.1 Variable Temperature STM



Figure 9: Variable Temperature STM: (a) Ultra-high vacuum system: Color code: green: load lock chamber, red: measurement chamber and yellow: molecule deposition chamber (from [46] with permission). (b) Tip holder with a tip inserted. (c) Schematic illustration of the STM core of the the STM Aarhus 150. (from manual of STM 150 Aarhus, with permission [47])

The real-space images were acquired by scanning tunneling microscopy (STM). The STM is part of the ultrahigh vacuum (UHV) system (Fig. 9a) with a base pressure better than 4×10^{-10} mbar. The UHV system consist of three chambers: the load-lock chamber (green), measurement chamber (red), and molecule deposition chamber (yellow) (Fig. 9a). The system is capable to perform usual UHV sample preparation such as Ar⁺ ion sputtering and annealing. After sample preparation, the sample is transferred into the STM from the preparation stage via a transfer rod.

The system equipped with a variable temperature STM (STM 150 Aarhus, SPECS), which includes a scanner platform (Fig. 9b) that the sample is inserted into for measurement. The scanner platform is connected to a liquid nitrogen (LN₂) flow-through cryostat via a copper braid. It provides the cooling ability down to ~110 K. The tip is attached to the tip holder, which is well-fixed by a clamp on the scanner tube (inset in Fig. 9b). The etched tungsten tip is mounted to the tip holder. It can be further cleaned by *in-situ* tip sputtering.

The STM consists of a single tube scanner for three-dimensional motion during scanning and an inchworm motor for the coarse approach (Fig. 9c). With this design the microscope can operate with fast scanning speed (from 1 images/min to 4 images/min) for all measurements described in this thesis in a temperature range from 130 K to 200 K. In addition, the STM has an approach speed of less than 1 mm/min with a maximum scan range of 1500 nm \times 1500 nm.



3.2 UHV Analysis System

Figure 10: UHV analysis system (SPECS). Orange frames: chambers, red frames: equipment.

The UHV analysis system (Fig. 10, *SPECS*) is equipped with a hemispherical analyzer (PHOIBOS 100, *SPECS*) for acquiring photoemission spectra. The system is mounted in a UHV chamber with a base pressure better than 8×10^{-10} mbar, which consists of several chambers for different purposes: the load-lock chamber, the preparation chamber, and the analysis chamber. The load-lock chamber is built for transferring samples from ambient to UHV conditions without venting the UHV part of the system. The preparation chamber is capable of sample preparation such as Ar⁺ ion sputtering and annealing, and a LEED for investigate the long-range order of the sample. The sample preparation

and measurement is done on a manipulator. The analysis chamber is equipped with a hemispherical analyzer, X-ray source, and UV source for surface investigation.

To determine the long-range order of the sample surface, I installed an MCP-LEED (BDL 800 IR-MCP, *OCI Vacuum Microengineering Inc.*) in the preparation chamber. The LEED is capable of operating with a low electron beam current down to a few nA to minimize the electron-induced reaction on the surface while probing the surface structure. The intensity of the diffraction pattern is further enhanced with a multichannel plate (MCP) by applying an accelerating voltage of 0.1 kV-1.0 kV.

For a clean deposition without affecting too much contaminating too much the preparation and analysis chamber, I installed a molecule deposition chamber. The molecule deposition chamber is equipped with a manipulator for transferring a doser to approach as close to the sample surface as possible (approx. 7 cm). I used it to deposit molecules such as water. The molecule deposition chamber is connected with the preparation chamber via a gate valve, it is opened when the deposition start.

3.2.1 X-ray Source

The x-ray source of the UHV analysis system is a dual anode x-ray tube (XR 50, *SPECS*) with Al and Mg as anode target materials. The anode is bombarded with high-energy electrons (10 keV to 15 keV) generated by cathode filaments (Fig. 11), the anode is cooled by water in order to prevent melting. Some of the electrons in core levels are removed, leaving vacancies in the energy levels. If these vacancies are refilled by electrons from energetically higher energy levels, characteristic x-ray radiation is generated.



Figure 11: Schematic view of the x-ray source (XR 50) (from manual of XR 50 [48] with permission).

3.2.2 Ultraviolet Source

The ultraviolet (UV) light is generated by the UV source (UVS 10/35, *SPECS*) with the gas helium (He) discharged (Fig. 12). The discharge pin is designed as a point anode and extends into the discharge capillary. It is based at a high voltage (~1.7 kV) which caused a discharge that is trapped in the capillary. At first the He gas is passing a differential pumping stage consisting of a membrane pump P1 and a turbo molecular pump P2 in order to achieve a pressure down to (~2 × 10⁻⁸ mbar). In this work, the photon energy of 21.22 eV (He–I) is chosen for measurement.



Figure 12: Schematic view of the UV source (UVS 10/35) (from manual of UVS 10/35 [49] with permission).

4 Experimental Methods

4.1 Preparation of Ag(111)

The Ag(111) single crystal (*MaTek*) was cleaned in both chambers by Ar⁺ ion sputtering at room temperature and annealing to 850 K to 900 K via electron bombardment at UHV conditions (Table 1). The sputtering sample current is significantly higher in the UHV analysis system than in the STM system, which is due to the difference of the sputtering spot diameter. In the UHV analysis system, the spot diameter is ~14 mm and the sample diameter is 8 mm, resulting in an effective emission current of ~5 μ A to 7 μ A. The Ag(111) sample is first sputtered for 10 min to 30 min followed by annealing for the same time, with the last cycle being shorter (5 min sputtering and 5 min annealing). The sample cleanliness was checked by STM, LEED, and XPS.

	Aahrus STM system	PES analysis system	
	Sputtering		
Ion Energy (keV)	1.3	1.3	
Sample Current (μA)	3-5	17-19	
Pressure (mbar)	3×10^{-5}	3×10^{-6}	
	Anne	ealing	
Accelerating Voltage (kV)	1.0	1.0	
Emission Current (mA)	15-17	16-18	

Table 1: Parameters for sample preparation.

4.2 Deposition of ZnO on Ag(111)

The growth of ZnO on Ag(111) was achieved by Zn evaporation on Ag(111) in the presence of O₂ (p ~ 5 × 10⁻⁶ mbar) at room temperature followed by annealing at ~600 K in UHV (p ~ 5 × 10⁻⁹ mbar) for 10 min. Zn was evaporated via an electron-beam assisted evaporator (EFM-3s, *Omicron*) from a rod material (*Goodfellow*, 2.0 mm diameter, 99.99% purity) at 450 V with an emission current of ~1.6 mA, resulting in a deposition rate of ~1 ML/hr. The evaporation material was outgassed under UHV conditions until the pressure stayed below 5.0×10^{-9} mbar. The coverage of the ZnO was determined by STM and is specified in percentages of the surface area covered. In this work, the ZnO covered between 15% to 75% of the Ag surface. In photoemission measurements, there was no clear indication for ZnO coverages. Here, the coverages of ZnO are therefore described by the overall deposition times to get the relative coverage. In this work, the ZnO coverages range from 5 min to 60 min.

4.3 Deposition of D_2O

The D₂O (Sigma-Aldrich, 99.99% isotopic purity) was filled into a glass tube that is connected to the UHV chamber via a leak valve. The D₂O was further purified in vacuum by several freeze-pump-thaw cycles. For the deposition, the leak valve was opened to reach the desired pressure $(1 \times 10^{-7} \text{ mbar})$ in the deposition chamber. During depositing, the sample was kept at a temperature around (130 ± 5) K in the STM system, and at ~90 K in the UHV analysis system. For the photoemission measurements, the coverage of D₂O was determined by the exposing time at a same exposing pressure. There are two definition for the D₂O coverages in this thesis to determine the D₂O coverages for fitting different topics. While discussing the water nucleation on the pristine ZnO, the coverage of D₂O, as determined by STM, is given as a percentage of the total surface area (Ag plus ZnO) covered, reflecting the importance of the pristine Ag for thee nucleation at the island border. In this work, the coverage of D₂O ranges from 6% ML to 70% ML. While discussing the water nucleation on the ZnO pre-covered with Cs^{$\delta+$} ions, the coverage of D₂O is given as a percentage of the ZnO surface area covered. In this work, the coverage of D₂O ranges from 6% ML to 85% ML.

4.4 Deposition of Cs

Cs was deposited from an alkali-metal dispenser (SAES) heated to ~1000 K onto the sample that was at a temperature of (230 ± 15) K. Before each deposition, the dispenser was degassed and then kept at ~1000 K for 5 min to reach a constant deposition rate. The unit cell coverages of the $Cs^{\delta+}$ ions are given as the percentage of the unit cells of the ZnO moiré pattern occupied by $Cs^{\delta+}$ ions. Thereby, only the surface covered by ZnO is taken into account. In this work, the unit cell coverages of $Cs^{\delta+}$ ions ranges from 26% to 87%.

4.5 Simulation

The simulation were done by Dr. Duy Le from the Department of Physics, University of Central Florida. The calculations were performed by using density functional theory (DFT) as implemented in the Vienna *ab initio* Simulation Package (VASP) [50] employing the projector-augmented wave (PAW) [51, 52] and the plane-wave basis set. The generalized-gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) [53, 54] functional together with DFT-D3 correction [55] is used to describe the electronic exchange-correlation. The electron kinetic energy cut-off for plane-wave expansion was set to 500 eV. To mimic the experimentally observed structures of the moiré periodicity of graphitic ZnO on Ag(111), which is (7×7) -ZnO/(8×8)-Ag(111), we constructed a model supercell with a 5 layer (8×8) Ag(111) slab on one side of which we placed a (7×7) monolayer of graphitic ZnO at a starting distance of about 250 pm and a vacuum of about 1500 pm that separated the periodic image of the model system along the direction normal to the surface. The monolayer is representative for the graphitic ZnO(0001) structure that grows in this form up to 2 ML [3]. It is a suitable model system for the bilayer, investigated experimentally, at reasonable computational cost. The dipole corrections [56, 57] along the direction of the surface normal was used to cancel the effects of an artificial uniform electric field created by the asymmetric model system. All structures were relaxed until all components of forces acting on each atom were less than 0.1 eV/nm, except for those in the bottom two Ag layers, which were held fixed. We sampled the Brillouin zone with one point at the zone center and used Gaussian smearing with $\sigma = 0.1$ eV for structural relaxation. All electronic cycles were converged to 10^{-2} meV. The binding energy of H₂O on the model surface was evaluated using $E_b = (E_{sys} - E_{surf} - nE_{H_2O})/n$, where E_{sys} , E_{surf} , and E_{H_2O} are the total energies of the considered system, the surface, and the H₂O in isolated form (which is evaluated in an $1.5 \times 1.5 \times 1.5$ nm³ box), respectively, and n is the number of molecules in a supercell. Simulated STM images were approximated to be the iso-surface (10^{-3} e/nm^3) of the local density-of-states (LDOS) of all occupied states between the Fermi level and the simulated bias. The resulting images were convoluted with a Gaussian filter with a standard deviation of 0.1 nm to mimic the effect of the finite size of the STM tip.

5 Results and Disscussion

This chapter is divided into four sections with the growth and properties of ultrathin ZnO films on Ag(111), the hydration of the moiré pattern of graphitic ZnO, the growth of Cs on the moiré pattern of graphitic ZnO, and the hydration of Cs on the moiré pattern of graphitic ZnO.

5.1 Growth and Properties of Ultrathin ZnO Films on Ag(111)

When selecting a surface for studying the oxide substrate support, oxide single crystals are an obvious choice. However, their broad bandgap and their insulating property restrict or even prevent the electron-based spectroscopy and microscopy, such as LEED, XPS, and STM measurements. Other issues are connected to sample cleaning under UHV conditions or are caused by inadequate thermal conductivity. Therefore, as an alternative method, the growth of ultrathin oxide film on metal support arises. It is proven that with a thickness of a few angstrom, an ultrathin oxide film can retain its physical properties of the bulk material [58]. Thus, in this chapter, we discuss the growth and oxidation of Zn on Ag(111) and further discuss the structure and electronic properties of the ultrathin ZnO film grown on Ag(111).

5.1.1 Oxidation of the Zn on Ag(111)

The first well-ordered zinc oxide ultrathin films on Ag(111) were grown by pulsed laser deposition of zinc oxide followed by an UHV annealing at a temperature up to 680 K [3]. In this work, physical vapor deposition has been used to deposit zinc. For examining the oxidation of the Zn on Ag(111), Zn was deposited for 30 min onto Ag(111) at room temperature. The surface is further exposed to an oxygen atmosphere (2×10^{-6} mbar) at room temperature followed by post annealing at ~600 K for 10 min at a pressure below $p = 5 \times 10^{-9}$ mbar. Each step is investigated by XP spectroscopy with an excitation energy of 1486.6 eV (Al K_{α}).

After depositing Zn for 30 min on Ag(111), two symmetric peaks at 1021.4 eV and 1044.4 eV evolve, which are assigned to Zn $2p_{3/2}$ and Zn $2p_{1/2}$ respectively (Fig.13a). After exposing it to oxygen atmosphere and post annealing at 600 K for 10 min, the Zn $2p_{3/2}$ peak shifts from 1021.4 eV to 1021.2 eV (Fig.13a) due to the interaction in the oxide. Furthermore, a peak appears in the O 1s region at a binding energy of 529.8 eV (Fig.13b). The presence of the O 1s peak indicates the oxidation of the deposited Zn on Ag(111). To confirm the oxidation of Zn on Ag(111), the Auger spectra of Zn LMM was recorded. After depositing Zn for 30 min, the presence of the broad Zn L₃M₄₅M₄₅ peak at a maximum of 494.2 eV is observed (Fig.13c). Further adsorbing oxygen and post-



Figure 13: Oxidation of Zn on Ag(111): XP spectra for (a) Zn 2p, (b) O 1s, (c) Zn LMM, and (c) Ag 3d. The XP spectra were excited by Al K_{α} ($h\nu = 1486.6$ eV).

annealing at 600 K leads to a +2 eV shift to a binding energy of 496.2 eV ($E_k = 990.4 \text{ eV}$). The difference in the binding energy of the Ag 3d peaks is less than 0.1 eV compared to the pristine Ag(111). The Ag 3d_{5/2} peak remains symmetrical and at a binding energy of 368.3 eV (Fig. 13d). Hence, charging of the sample could not account for the shift of +2 eV observed in the Zn LMM Auger spectra (Fig. 13c), but the oxidation of the adsorbed Zn forming a layer of ZnO. After oxidation of the surface Zn, the Auger lines are significantly broadened (Fig. 13c). The broadening of the Auger lines are due to the different layers of ZnO, which have different structures. To determine whether the Zn is fully oxidized on the Ag(111) surface, we further compare the Zn to O ratio by integrating the peak area of Zn 2p_{3/2} and O 1s. The Zn to O ratio (R_{Zn-O}) is defined by

$$R_{Zn-O} = (I_{Zn \ 2p_{3/2}} / \sigma_{Zn \ 2p_{3/2}}) / (I_{O \ 1s} / \sigma_{O \ 1s})$$
(13)

where $I_{Zn \ 2p_{3/2}}$ and $I_{O \ 1s}$ refers to the integrated XP intensity, and $\sigma_{Zn \ 2p_{3/2}}$ and $\sigma_{O \ 1s}$ are corresponding cross-section values, which depend on the excitation photon energy $(h\nu = 1486.6 \text{ eV})$. The XP spectra for 30 min of ZnO was chosen and the Zn $2p_{3/2}$ and O 1s peaks were integrated. Taking $\sigma_{Zn \ 2p_{3/2}} = 0.3907$ and $\sigma_{O \ 1s} = 0.04$ into account [59], the R_{Zn-O} is determined to (0.95 ± 0.06) (Table 2). Thus, the Zn is fully oxidized on Ag(111).

Table 2: Zn to O ratio.

	$I_{Zn \ 2p_{3/2}}$	$\sigma_{Zn\ 2p_{3/2}}$	$I_{O \ 1s}$	$\sigma_{O\ 1s}$	\mathbb{R}_{Zn-O}
Values	255026 ± 4327	0.3907	27220 ± 1224	0.04	0.95 ± 0.06

5.1.2 Electronic Structure of the Ultrathin ZnO Film

After investigating the oxidation process of ZnO grown on Ag(111), we further compare the different coverages of ZnO. After 5 min deposition of ZnO, a small peak at 1021.2 eV appears in the core-level spectrum of Zn $2p_{3/2}$ (Fig. 14a). As the coverage increases, the peak becomes more intense but the binding energy of Zn $2p_{3/2}$ remain the same at 1021.2 eV. The O 1s spectra also have the same trend as Zn $2p_{3/2}$. A broad and low intensity peak appears at the binding energy of 529.8 eV after depositing 5 min of ZnO. This peak further increases its intensity without a shift in its binding energy with the coverage of ZnO (Fig. 14b). A similar trend as Zn $2p_{3/2}$ is also found on the Zn LMM Auger lines. Upon 5 min of ZnO deposition, a broad and less intense peak appears at the binding energy of 496.2 eV ($E_k = 990.4 \text{ eV}$) (Fig. 14c). The intensity of the Zn LMM Auger spectra increases with the coverage of ZnO. These increases in intensity are all related to the increase in the amount of surface ZnO. On the other hand, the increase of the ZnO coverage leads to a decrease in intensity of the Ag 3d signals (Fig. 14d). The Ag $3d_{5/2}$ peak is most intense at the pristine Ag(111) surface, and centered at 368.3 eV. As the coverage increase, the intensity of the Ag $3d_{5/2}$ attenuates, further indicating the increasing in ZnO coverage.

Having presented the core-level spectra of the ZnO/Ag(111), we now turn to investigate their Shokley-type surface state with varying ZnO coverages, which was measured close to zero binding energy with a photon energy of 21.2 eV. On pristine Ag(111), a clear and symmetrical peak centered at a binding energy of 67 meV is observed (Fig. 15a), which is assigned to the Shokley-type surface state of Ag(111) [60]. Deposition of 5 min of ZnO on Ag(111) leads to a broadening and a slight asymmetry of the original peak, indicating that a new peak appears in the spectrum. The spectrum of 60 min deposition of ZnO on the Ag(111) was fitted with a known peak position of the surface state of Ag(111) at 67 meV, which reveals a new peak at 154 meV. Thus, every spectrum was further



Figure 14: Coverage dependence of ZnO on Ag(111): XP spectra for (a) Zn 2p, (b) O 1s, (c) Zn LMM, and (d) Ag 3d for different ZnO deposition time. The XP spectra were excited by Al K_{α} ($h\nu = 1486.6$ eV).

fitted with these two peaks at 67 meV (blue curve in Fig. 15a) and 154 meV (red curve in Fig. 15a). The peak centered at 154 meV gains more intensity as the ZnO coverage increases, meanwhile, the intensity of Ag(111) surface state decreases. This observation is further confirmed by integrating the peak area (Fig. 15b). The peak area of the Ag(111) surface state (blue square) is the largest at the pristine surface, and it decreases to around 1/3 of its original peak area after depositing 60 min of ZnO. After this 60 min of ZnO deposition, the surface state of the Ag(111) still appears in the spectrum, indicating that even at this coverage there is still uncovered Ag(111) remaining on the surface. The peak area of the red curve increases with the ZnO coverages. This trend of increasing peak area with the ZnO coverage suggests a relationship with ZnO. However, a previous UPS



Figure 15: Shockley-type surface state of ZnO/Ag(111): UP spectra for (a) surface state as a function of the deposition time of ZnO, colored dashed lines represent two fitted curve at 154 meV (red) and 67 meV (blue). (b) Integrated peak area from (a). The UP spectra were excited by He–I ($h\nu = 21.2$ eV).

study for bulk ZnO(0001)-Zn does not have a signal in this region [61]. Thus the peak centered at 154 meV should come from the growth of the interface state between ZnO and Ag(111), which increases with the amount of Ag(111) covered by ZnO.

5.1.3 Structure and Ordering of the Ultrathin ZnO Film

After studying the property of ZnO by photoemission spectroscopy, we turn to investigate the structure and the ordering of the ZnO. To observe the long-range ordering, the LEED patterns were recorded. The pristine Ag(111) surface shows a hexagonal set of diffraction spots (Fig. 16a). This set of sharp and intense diffraction spots indicates a clean and ordered surface of fcc(111) orientation. Upon depositing 5 min of ZnO onto the Ag(111) surface, another hexagonal set of dim diffraction spots appears (Fig. 16b) closer to the center (red arrow in inset of Fig. 16b), while the Ag(111) spots become slightly less intense. These set of new hexagonal spots are assigned to the ordered ZnO structure. After depositing 35 min of ZnO, the Ag(111) spots turns more gloomy whereas the ZnO spots get more intense (Fig. 16c, and red arrow in inset). At the highest coverage after depositing 60 min of ZnO, the diffraction pattern of ZnO is stronger than the Ag(111) (Fig. 16d, and red arrow in inset). In addition, the ZnO diffraction spots also become more diffuse upon deposited 60 min of ZnO, probably due to the order slightly reduced on higher ZnO



Figure 16: Long-range ordering of ZnO: The LEED pattern of (a) pristine Ag(111), deposition of (b) 5 min of ZnO, (c) 35 min, and (d) 60 min of ZnO. Insets are the magnified images of the squared area in every images. Red arrow: the diffraction pattern of ZnO. The electron beam energy is 89 eV with the MCP voltage of 0.8 kV. All diffraction patterns are converted into gray scale and colors are inverted.

layers. Surface x-ray diffraction (SXRD) measurements [3] determined that ZnO grows in the (0001) orientation on Ag(111) aligned with the Ag(111) symmetry.

To understand the geometrical structure of the ultrathin ZnO film, the STM is used to study its structure in real-space. The Zn deposited onto the Ag(111) has a possibility to intermix between Zn and Ag on surface [4], therefore, a presence of oxygen during deposition was used to suppress the intermixing of Zn and Ag. To reduce the intermixing between Zn and Ag, from now on, the deposition of Zn is thus under an oxygen atmosphere $(p = 5 \times 10^{-6} \text{ mbar})$ to avoid the surface intermixing, followed by annealing at 600 K under UHV for 10 min. After deposition, a well-ordered layer of ZnO forms on the Ag(111)



Figure 17: Structure and ordering of ZnO: STM images of (a) 84% of ZnO on Ag(111), inset enlarged by a factor of five, (b) atomic resolution of ZnO moiré pattern, and (c) the height profile along the red line in (b). (d) Contrast enhanced LEED images for deposition of 60 min of ZnO on Ag(111). (e) DFT optimized structure of a single-layer of ZnO(0001)–(7 × 7)/Ag(111)–(8 × 8); color code: Ag: gray, Zn: yellow, and O: red. (f) Simulated STM image of ZnO moiré pattern on Ag(111) with a tunneling voltage of 1.5 V. Scanning parameters: (a) $V_t = 1.3$ V, $I_t = 170$ pA, RT, and (b) $V_t = 0.2$ V, $I_t = 70$ pA, RT. Imaging parameters: (d) electron beam energy is at 77 eV, with the MCP voltage of 0.8 kV; the diffraction pattern is converted into gray scale and the color is inverted.

surface (Fig. 17a). The periodic protrusions on the ZnO layer are the moiré pattern, which is commonly assigned to the lattice mismatch between Ag(111) and ZnO(0001) (inset in Fig. 17a). The atomic resolution of the moiré pattern reveals a hexagonal structure (Fig. 17b), which is in a good agreement with our LEED patterns (Fig. 16). The smaller round protrusions in the atomic resolution image (Fig. 17b) are most likely the oxygen atoms since the oxygen atoms have more valence electrons. The height profile across two moiré structures along the red line was measured to determine the lattice constant of the ZnO layer. The unit cell length of the moiré structures is ~2.3 nm. In this range, there are seven intervals that correspond to a lattice constant of ZnO of ~330 pm (Fig. 17c).

We also observe a set of dim, hexagonal diffraction patterns surrounding the diffraction pattern of ZnO after the contrast enhancement (black rhombus in inset in Fig. 17d). These extra spots are assigned to the moiré pattern of the ZnO. These hexagonal spots do not appear for the deposition of ZnO below 60 min, this could be because the amount of the moiré structure is not enough at this deposition time to show on the diffraction pattern. Combining the long-range ordering obtained through LEED, the localized structure gained by STM, and the previous study of ZnO growth on Ag(111) [3,4] and Au(111) [5], we can determine the ordering here as a $ZnO(0001) - (7 \times 7)/Ag(111) - (8 \times 8)$ coincident structure. In order to identify the different regions as imaged by STM, we perform a DFT calculation for a single-layer ZnO(0001) adsorbed on Ag(111). At all thicknesses below 2 ML, thin films of ZnO(0001) grown on Ag(111) exhibit a graphitic structure [3]. Thus, we consider a monolayer a good approximation to mimic the experimental bilayer graphitic ZnO thin film. The moiré pattern of ZnO comprises three highly symmetric regions related to the highly symmetric adsorption sites of Ag(111) (Fig. 17e). At the hcp region, one Zn atom adsorbed near an hcp site of Ag(111) is framed by three O atoms adsorbed near atop sites (hcp in Fig. 17e). At the fcc region, one Zn atom adsorbed near an fcc site of Ag(111) is framed by three O atoms adsorbed near hcp sites (fcc in Fig. 17e). At the atop region, three Zn atoms are adsorbed near atop sites of Ag(111), forming a hexagon with three O atoms that are adsorbed near fcc sites. The hexagon encircles an hcp site of the Ag(111) (atop in Fig. 17e). Based on the calculated ZnO moiré pattern, we simulated an STM image to compare its local density-of-states. The STM image is simulated at the tunneling voltage of 1.5 V that is mostly used in our STM measurement of the pristine ZnO surface. In the simulated STM image, the hcp regions exhibit the highest local density-of-states (LDOS), followed by the atop regions and the fcc regions of the ZnO moiré pattern (Fig. 17f). These results are attributed to the structure of the different regions. The DFT calculations suggest that the ZnO bilayers are atomically flat and that the moiré structure resulting from the corrugation of the LDOS (Fig. 17e,f) is due to the lattice mismatch between ZnO and Ag(111) [4,5]. Since O atoms contribute more states than Zn atoms near the Fermi level [5], the region of the ZnO moiré pattern configured with O atoms adsorb on atop sites of Ag atoms, i.e., hcp regions of the moiré pattern, gives the highest local LDOS, resulting in the highest protrusions in STM imaging. The lowest depressions are from the most mismatched position in the unit cell of the moiré pattern due to the lowest LDOS, where Zn and O atoms are both adsorbed at the hollow sites of Ag(111), i.e., the fcc regions of the moiré pattern. The intermediate regions are then attributed to the atop region of the moiré pattern.

5.1.4 Summary

With the help of various surface probe techniques, we summarize the growth of the ultrathin ZnO film on Ag(111) by using physical vapor deposition of Zn and oxidation. On the Ag(111), the crystalline ZnO film is formed after deposition in an oxygen atmosphere and post-annealing at ~600 K for 10 min. The Schockley-type surface state of the Ag(111) does not vanish after 60 min of ZnO growth, indicating that there are still uncovered Ag(111) remaining on the surface even at this coverage. Moreover, the intermediate state between ZnO and Ag(111) appears, pointing out some metallic properties of the ultrathin ZnO film. This ultrathin ZnO film has an orientation of (0001) [3] with a unit cell length of the moiré pattern of ~2.3 nm. The lattice constant of the ultrathin ZnO film is ~330 pm, which is close to the lattice constant of the bulk ZnO(0001) with a lattice constant of 325 pm. The close lattice constant of the ultrathin ZnO oxide film on Ag(111) further emphasizes that the ultrathin oxide film retains the physical properties of the bulk material [58].

5.2 Hydration of the Moiré Pattern of Graphitic ZnO

After discussing the structure and properties of the ultrathin ZnO film supported by the Ag(111), we turn to study one of the reacting substances in the water gas shift reaction, which is water. The first step in the reaction mechanism of the heterogeneous catalysts is the adsorption of reactants. We investigate the water adsorption and distribution on the supported ultrathin ZnO film with STM, and further discover the reaction mechanism of water on the ZnO with XPS.



5.2.1 Inhomogeneous Distribution of Water Clusters on ZnO

Figure 18: Coverage dependence of D₂O on ZnO islands: (a to c) STM images at local coverages of (a) 7% ML, (b) 10% ML, and (c) 14% ML; region in yellow frame enlarged by a factor of 2 in panel (a). (d) Percentage of hcp regions on ZnO moiré pattern occupied by D₂O clusters for different parts of the border of the island as labeled in panels (a), (b), and (c). The STM images were all recorded at $V_t = 1.5$ V and (a) $I_t = 180$ pA, (140 ± 1) K, (b) $I_t = 140$ pA, (143 ± 1) K, and (c) $I_t = 130$ pA, (159 ± 1) K.

 D_2O at a local coverage between 7% ML to 14% ML forms clusters on the ZnO islands of the partially covered ZnO/Ag(111) surface (Fig. 18). Here, we discuss the distribution of D_2O on the metal and the supported oxide surfaces. The coverage of D_2O is given as a percentage of the total surface area (Ag plus ZnO) covered. Two different cluster densities exist in Fig. 18a. At the interior of the ZnO islands, there is a low density of clusters (white arrows in yellow-bordered magnification in Fig. 18a). The border of the ZnO island is much more densely populated; the D_2O forms a rim of clusters along the island border (red arrows in Fig. 18a). In both parts, the D_2O clusters are exclusively nucleated at the protrusions of the ZnO moiré pattern, i.e., its hcp regions. This preference is confirmed by our DFT calculations (see below). At increasing local D_2O coverage, more clusters nucleate while their size hardly changes (Fig. 18b and c). Only a few additional clusters nucleate in the interior of the islands, while the cluster density at their borders increases more substantially, filling the second and third row of the moiré pattern from the island borders. This observation is quantified in a histogram of the percentage of the occupied hcp regions by D_2O clusters for the first three rows from the island borders (Fig. 18d). Also along these, the D_2O coverage is not homogeneous. In order to compensate for the different local coverages, we separate the islands into parts with different hcp region occupations of the three rows from the island borders. A STM image of the edge region of one of the ZnO island is used to clarify the definition of three rows from the ZnO island border (Fig. 19). A row of the moiré pattern is defined by the protrusions of the moiré structure, also known as the hcp regions of the ZnO moiré pattern (Fig. 17e), parallel to the border of the island edge (Fig. 19). Hence we define the outer-most three rows as the first (red), second (green), and third (blue) row in a distinct color within an STM image near the ZnO island border as an example (see Fig. 19). The D_2O occupation at the ZnO island border is given in percentage of the number of water-covered hcp regions parallel to this border. We compare the three rows closest to the island borders for six hcp region



Figure 19: Definition of rows of the moiré pattern from the edge: STM image of the nearborder ZnO island. Red: the first row, green: the second row, and blue: the third row. Scanning parameter: $V_t = 1.1$ V, $I_t = 100$ pA, RT.

occupations (Fig. 19d). In general, the individual occupation in every row increases with local hcp region occupation. The first row is occupied by around 60% for an hcp region occupation below 36% and more than 80% above 55% hcp region occupation. The second row is occupied by 16% at the lowest occupation of ~26%. The occupation doubles and triples for hcp region occupations of around 40% and above 55%, respectively. This trend continues for the third row, in which less than 20% of the hcp regions are occupied by D_2O clusters at an occupation below 55%. This points to an inward mass transport of water accumulated at the border to more interior parts of the islands with increasing local water coverage.



Figure 20: Distribution of D₂O accumulated at the borders of ZnO islands: (a) STM image at 4% ML local coverage of D₂O deposited at (130 ± 5) K, scanning parameters: $V_t = 1.5$ V, $I_t = 90$ pA, (144 ± 1) K. Yellow lines: borders of the capture zone, white lines: nearest distances between ZnO islands (b) relationship between the percentage of D₂O clusters occupying the hcp regions and the nearest distances between ZnO islands; squares: experimental data; red dashed lines: two linear regressions for increasing and saturation range.

To understand the highly inhomogeneous distribution along the island border, we point out that there are no D_2O clusters on the bare part of the Ag(111) surface at any of the examined D_2O coverages. We further recall that the temperature during deposition of ~130 K is below the desorption temperature of water from Ag(111) [62] but that the water molecules are highly mobile at this temperature [18]. We thus propose that the high density of water at the border originates from the water molecules adsorbed on the bare Ag(111) but nucleated at the border of the ZnO islands. For this scenario, the occupation of the hcp regions should depend on the capture zone around the ZnO islands. This proposition is verified for ZnO islands in close proximity. At a low local D_2O coverage of 4% ML, the first row of three ZnO islands is only partly covered by D_2O (Fig. 20a). Indeed, there are fewer D_2O clusters at the border of the ZnO islands facing other ZnO islands than at the other borders. To quantify this observation, we relate the occupation of the hcp regions at the borders of the islands to the nearest distance between two ZnO islands. The capture zone is approximated by constructing a Voronoi diagram [63] based on the center positions of the ZnO islands (Fig. 20a). In the capture zone, we measure the cluster density at that part of the border belonging to this zone. At increasing distance between two ZnO islands, the cluster density at the ZnO border increases from ~20% at ~7 nm distance to above ~80% at ~12 nm distance, above which it saturates (Fig. 20b). This dependence confirms that the high occupation of the hcp regions of ZnO by the water clusters at the ZnO island borders results from water molecules that were adsorbed on Ag(111), then diffused to a border of an island and onto it, and finally nucleated on hcp regions of the moiré pattern. At an increasing occupation of the hcp regions closest to the island borders, the molecules diffused on the islands to nucleate at more interior hcp regions.

5.2.2 Structure of Water Clusters on the ZnO/Ag(111)

Having understood the highly inhomogeneous distribution of the water clusters on the ZnO islands, we now turn to investigate their structure. At the island borders (Fig. 20a), as well as the interior of the island (yellow frame in Fig. 18a) and on almost closed ZnO layers (Fig. 21a and b), the size of the D₂O clusters is rather small and uniform up to coverages of around 70% ML. Only at this coverage and above, the D₂O clusters connect across hcp regions to form longer chains (Fig. 21c). The cluster growth is distinctly different from that on homogeneous surfaces such as Ag(111) at a similar temperature of (118 ± 3) K [18]. On homogeneous surfaces, water clusters grow larger with increasing coverage at almost constant cluster density [17–19] while here the cluster density increases.

For a geometric analysis, we concentrate on clusters that occupy one hcp region only. We characterize the close to circular D_2O clusters geometrically as exemplified in Fig. 21d. The diameter is measured as its broadest full width at half maximum (FWHM). The apparent height refers to the hcp-related protrusions of the moiré pattern. At a bias voltage of 1.5 V, the apparent height histogram hardly changes, ranging from 43 pm to 200 pm at an average of (108 ± 17) pm for the local coverage of 16% ML and (126 ± 18) pm for a local coverage of 37% ML (Fig. 21e). As there are no apparent heights reported so far for water clusters on oxide surfaces, we compare these values to the apparent heights measured on the coinage metal surfaces. The apparent heights of the D₂O clusters on ZnO measured here at 1.5 V are mostly larger than those of small single-layer clusters on coinage metal surfaces such as Au(111) (~90 pm) [16] and Cu(111) (~85 pm) [64], measured at -100 mV and 20 mV, respectively. As the apparent heights of amorphous and crystalline ice on Cu(111) increase at 58 pm/V and 40 pm/V, respectively [14], the

height is nonetheless consistent with single-layer clusters.

Likewise, the diameter of the D₂O clusters on ZnO depends only slightly on coverage, varying between 1.1 nm and 2.3 nm at an average of (1.63 ± 0.15) nm for the local coverage of 16% ML and (1.74 ± 0.16) nm for the local coverage of 37% ML (Fig. 21f). The range suggests that clusters of several sizes coexist, despite its being much narrower than on a homogeneous surface. The diameters are in the range of those measured with a molecular resolution for clusters of monolayer height on a related surface, the ultrathin FeO film (orange arrows in Fig. 21f). On both moiré patterned oxides, the clusters are distinctly different from islands grown on the homogeneous coinage metal surface [18,20]. To understand the preference of water adsorption on the hcp regions, we carried out DFT calculations of a water hexamer adsorbed on the three regions, i.e., hcp, fcc, and atop,



Figure 21: Coverage-dependent geometry of D₂O clusters on ZnO layers: (a to c) STM images for D₂O coverages of (a) 16% ML, (b) 37% ML, and (c) 70% ML (d) Height profile of a typical D₂O cluster at a local coverage of 16% ML on a ZnO hcp region along red line as marked in inset (e) apparent height and (f) diameter distribution for two coverages of 16% ML (green, N₀ = 65) and 37% ML (gray, N₀ = 98). White arrow in (c) marks the one-dimensional D₂O chain, black arrow in (f) marks the smallest D₂O clusters found on the ZnO moiré pattern; orange arrows mark the longest axes of water clusters on the ultrathin film of hydroxylated FeO (estimated from Fig. 3b in [8]). Scanning parameters: (a) $V_t = 1.5$ V, $I_t = 130$ pA, (159 ± 1) K, (b) $V_t = 1.5$ V, $I_t = 120$ pA, (143 ± 1) K, and (c) $V_t = 1.3$ V, $I_t = 330$ pA, (142 ± 1) K.

of the ZnO moiré pattern. The hexamer structure is similar to the stable structure for water hexamers on the low index coinage metals [16, 21–23] and ultrathin FeO film [8]. Our DFT calculation confirms that the water hexamer prefers to adsorb on the hcp region of the ZnO moiré pattern with binding energies per H₂O molecule of 0.735 eV, 0.705 eV, and 0.705 eV for the adsorption at hcp, fcc, and atop, respectively. The preference of the hcp region results from thus the higher density-of-state than other regions, promoting the formation of the hydrogen bond toward the surface O atoms.

In the hexamer structure, three of the water molecules bind directly to the surface Zn atoms via their O atoms (yellow in Fig. 22a), referred herein to as surface-bonded H_2O . The other three water molecules (green in Fig. 22a) are hydrogen-bonded to the surfacebonded H_2O molecules with one additional OH group each hydrogen bonding to nearby surface O atoms (white arrows in Fig. 22a). The hydrogen-bonded water molecules (green in Fig. 22a and b) are rotated such that their dangling OH groups point toward a surface O atom. Their hydrogen bonding results in an outward relaxation of this O atom (marked by white arrows in Fig. 22a). Its bonding strength is reflected in the rather short hydrogen bond length of 191 pm (h_3 in Fig. 22b). The hydrogen bonding distances between the water molecules alternate between 196 pm (d_1 in Fig. 22a) and 160 pm (d_3 in Fig. 22a). It leads to the six non-equal O–O distances in the water hexamer, alternating between 294 pm (d₂ in Fig. 22a) and 263 pm (d₄ in Fig. 22a). Both distances are smaller than the Zn–Zn distance of 329 pm, such that the adsorption sites of the water molecules are slightly shifted from the atop site of the Zn atoms. Moreover, the water molecules in the hexamer are not adsorbed at the same height above the surface. Instead, the three surface-bonded water molecules are closer to the surface than the other three with O-Zn distances of 221 pm (h_1 in Fig. 22b) and 298 pm (h_2 in Fig. 22b), respectively. This buckling by 77 pm is, remarkably, the same as a water hexamer on a metal, the Cu(111)surface, of 76 pm [21].

Similar hexameric structures develop on both hydroxylated and non-hydroxylated regions of ultrathin FeO films [8]. On the non-hydroxylated FeO, half of the water molecules of the hexamer bind to surface atoms and the other water molecules are hydrogen-bonded to them [8], as on ZnO. In contrast to the structure on ZnO, the surface-bonded water molecules bind via their OH groups to surface oxygen and not via their lone pairs to the metal. Moreover, the free OH of the hydrogen-bonded water molecules point towards vacuum for FeO, but form a weak hydrogen bond with a surface oxygen for ZnO. We relate these differences to the buckled structure of FeO, which suppresses binding to the iron. On the hydroxylated ultrathin FeO film, in addition to half of the water molecules in the hexamers forming OH groups to surface oxygen, the other half binds to the hydroxylated oxygen through their oxygen lone pair [8], stabilizing the hexamer. The hexamer leads to a round protrusion in a simulated STM image with a diameter of ~ 1.0 nm (yellow arrow in Fig. 22c), very close to the smallest water cluster in experiments, at a diameter of ~ 1.1 nm (Fig. 22d). Both shapes are circular, thus, confirming that the smallest D₂O cluster on the ZnO is a hexamer on the hcp region of ZnO (Fig. 22d). Only very few clusters exhibit this smallest size at the investigated coverages (black arrow in Fig. 21f). Larger water clusters on hydroxylated FeO thin films form via combining



Figure 22: Structure of water hexamer on hcp region: DFT-calculated structure in (a) top and (b) tilted view, color code: blue: Zn atoms, red: O atoms from ZnO, yellow: O atoms from water bound to Zn atoms, green: O atoms from hydrogen-bonded water, and white: H atoms. d_1 , d_3 , and h_3 are the hydrogen bond distances, d_2 and d_4 are the O–O distances between the water molecules, h_1 and h_2 are the heights of the water O atoms above the surface Zn atoms; white arrows point to the hydrogen-bonded surface O atoms (c) Gaussian-filtered simulated STM image of seven water hexamers on hcp regions of the ZnO moiré pattern at a tunneling voltage of 1.5 V; yellow arrow points out a water hexamer (d) STM image of the smallest D₂O cluster at the same scale and same voltage as (c), scanning parameters: $V_t = 1.5$ V, $I_t = 130$ pA, (142 ± 1) K.

several water hexamers [8]. However, our DFT results reveal that two combined water hexamers are unstable because of the smaller distance between two oxygen atoms in the water hexamers than that between Zn atoms in the ZnO layer. Though of similar size, the larger D_2O clusters on ZnO are thus structured differently than those on hydroxylated FeO thin film, presumably due to the stabilizing effect of the direct binding of all water molecules to the surface.

We finally point out three major differences in water nucleation on ultrathin ZnO as compared to ultrathin FeO. First, the water clusters nucleate and grow exclusively at the hcp regions of the ultrathin ZnO film (Fig. 21a and b) up to a local water coverage of $\sim 70\%$ ML, but they form extended islands on the bare ultrathin FeO film already at low coverage. Only on the hydroxylated ultrathin FeO film, small and separated water clusters are confined to the fcc domains of the moiré pattern [8]. It implies that on the non-hydroxylated FeO ultrathin film, the energy difference between different regions is considerably smaller than on the ZnO ultrathin film.

Second, the water clusters nucleate on the fcc regions of the hydroxylated FeO moiré pattern [8], but on the hcp regions of the ZnO moiré pattern. On the hydroxylated domains of the FeO moiré pattern, the water structures are stabilized by three water molecules accepting hydrogen bonds from surface hydroxylated oxygen [8]. The FeO film is more hydroxylated at its fcc region than on other regions, explaining the preference of water to nucleate on these regions.

Third, the water hexamer on the ZnO ultrathin film is, at 77 pm, more buckling than on the FeO ultrathin film with 10 pm to 25 pm, at least on the hydroxylated one, for which a value is stated in [8]. Both types of water molecules are differently bound to the two oxide surfaces. The ones binding through their lone pair (yellow in Fig. 22a) bind to the metal of the ZnO but to a hydroxyl of the FeO. The hydrogen bonds of the ones binding through the hydrogen bond is shorter on FeO than on ZnO, resulting in a stronger hydrogen bonding. A more similar bonding of all of the water molecules to the FeO than ZnO surface results in a flatter structure of the water hexamer.

5.2.3 Photoemission Observation of Water Adsorption on ZnO/Ag(111)

Having discussed the structure and distribution of water clusters on graphitic ZnO, we look further into the XP spectra to trace the reaction of water. We first deposit D_2O at ~90 K onto the pristine Ag(111) surface as a reference. No signal is found in the O 1s region while investigating the pristine Ag(111), indicating a clean surface after sputtering and annealing (Fig. 23a). Upon depositing 60 s of D_2O , a small signal at a binding energy of 533.4 eV rises (Fig. 23a), confirming the presence of D_2O on Ag(111). The O 1s spectra are further processed with a Gaussian fit to determine the peak positions and the peak areas (red lines in Fig. 23a). Increasing the D_2O coverage leads to a linear increase in its intensity with coverage (Fig. 23b) with the peak position remaining the same at 533.4 eV (Fig. 23a), indicating that the chemical environment of D_2O molecules on the Ag(111) surface is the same. At high D_2O coverage, due to the surface being fully covered by D_2O molecules, we expect the value of 533.4 eV to represent a water-water interaction for D_2O adsorption on Ag(111).

After depositing 60 min of ZnO onto the Ag(111), a symmetrical peak is forming in the O 1s region centered at 529.8 eV (Fig. 24a). This is the formation of ZnO which was discussed in section 5.1.1. After depositing D₂O for 60 s, a broad peak with a binding energy centered at 532.4 eV appears in the O 1s region (Fig. 24a), which is assigned to water adsorption on ZnO. Upon increasing the D₂O coverage, the water signal further blue shifts to 532.9 eV (Fig. 24a). Comparing to the binding energy for D₂O adsorption on Ag(111), which is 533.4 eV (Fig. 23a). Thus confirms the previous finding that the D₂O nucleate on the ZnO instead of on Ag(111) (section 5.2). While increasing the D₂O coverages, the binding energy of the water layer is getting closer to the pure water-water interaction as on Ag(111) (533.4eV) (Fig. 24), indicating the increasing water-water inter-action between D₂O molecules. The water signal vanishes after warming up the surface



Figure 23: Coverage dependence of D_2O on Ag(111): (a) O 1s spectra for different coverages of D_2O on the Ag(111), red lines represent the Gaussian fits. (b) The integrated area of the fitted curve, red dash line represent a guiding line.

to room temperature (Fig. 24a), indicating full desorption of water from the ZnO at room temperature. The spectra are further fitted with two Gaussian peaks to determined their intensities. Increasing the D₂O coverages leads to a increasing of the D₂O intensity in the O 1s region (red in Fig. 24b), while the intensity of the oxide decreased to around three-quarters from the origin (blue in Fig. 24b). The increase in the D₂O coverage also increase the escaping length of the excited electrons from the ZnO, hence the intensity decreases with increasing D₂O coverage. After warming up the surface to room temperature the signal of ZnO recovered further suggesting this interpretation (blue dot at 300 K in Fig. 24b).

The desorption of larger amounts of water on Ag(111)-supported ZnO is also traced by XPS. After depositing 60 min of ZnO on the Ag(111), a small shoulder of the ZnO at 532.1 eV is present in the O 1s spectrum which is assigned as surface hydroxyl groups forming with hydrogen or water from the residual gas after comparing the water adsorption on planar ZnO supported by Au(111) [65]. However, the Ag(111)-supported graphitic part of the ZnO does not contain hydroxyl groups, not even upon depositing water to the surface [9]. From section 5.2, we further know that the water clusters do not nucleate on Ag(111). Thus, we deduce that the hydroxyl groups are adsorbed on higher layers of



Figure 24: Coverage dependence of D₂O on Ag(111)-supported ZnO: (a) O 1s spectra for different coverages of D₂O on the Ag(111)-supported ZnO. (b) The integrated area of the fitted curve. The blue and red line in (a) are the Gaussian fitted curve. Color code: red: D₂O, blue: ZnO.

the ZnO, which are not graphitic, which are present close to monolayer formation (see Fig. 17).

After adsorbing 8 min of D_2O at ~90 K, a broad signal at 533.5 eV appears in the O 1s region (Fig. 25a), which is assigned to the D_2O on the graphitic ZnO and the higher layer of ZnO. The binding energy of 533.5 eV on ZnO is close to the 533.4 eV on Ag(111) (Fig. 23a), which suggests a water-water interaction similar to on Ag(111). Since the binding energy of submonolayer water on ZnO is at 532.9 eV (Fig. 24a), the signal at 533.5 eV is the multilayer D_2O adsorption on the ZnO layers. After annealing the surface to ~170 K, the binding energy of D_2O shifts from 533.5 eV to 532.8 eV (Fig. 25a) while the intensity decrease to half of its original value (Fig. 25b), which is due to the desorption of the multilayer D_2O from the surface. Increasing the temperature to 200 K leads to a shift to 532.4 eV. Another peak shift to 532.1 eV is observed after increasing the temperature to 300 K (Fig. 25a). Since the signal with a binding energy of 532.1 eV corresponds to the adsorbed hydroxyl group from the non-graphitic layer of ZnO [65], the signal at the binding energy of 532.4 eV in the temperature range from 200 K to 300 K is the monolayer water and the surface hydroxyl group coexisting state. Note that the surface hydroxyl



Figure 25: Temperature dependence of D₂O interaction on Ag(111)-supported ZnO: (a)
O 1s spectra for depositing 8 min of D₂O on the Ag(111)-supported ZnO and further annealed to selected temperatures. (b) The integrated area of the water signal. The color code for the Gaussian fit in (a): red: D₂O/intermediate/hydroxyl group, blue: ZnO.

group will not form on the graphitic part of the ZnO [9], suggesting that the intermediate state only appears on the non-graphitic part of ZnO. The surface hydroxyl group desorbed slightly upon annealing the surface further to 400 K and 500 K (Fig. 25b). Previous work for D₂O interaction with planar ZnO supported by Au(111) suggests that the surface hydroxyl group desorbed at around 600 K [65]. Thus, we deduce that annealing the water adsorbed on the Ag(111)-supported graphitic ZnO leads to desorption of multilayer at ~170 K and the monolayer at ~200 K. On the non-graphitic part of ZnO, the coexisting state is found at ~200 K. Annealing to ~300 K leads to the formation of surface hydroxyl groups, and finally the complete desorption at ~600 K.

5.2.4 Summary

Based on various surface probe techniques, we summarize the growth and distribution of water on a graphitic ZnO ultrathin film. Water molecules adsorbed on the Ag(111) surface diffuse to the ZnO border followed by upward transport from the metal to the metal-oxide border, where they nucleate on the energetical preferred hcp regions of the ZnO moiré pattern along the border. The cluster density along the ZnO island border depends on the amount of Ag surface exposed to that border. The water also undergoes inward mass transport to more interior parts of the ZnO island and nucleates at the energetical preference hcp regions of the ZnO moiré pattern. Ab initio calculations suggest that the basic structure of the water clusters is a water hexamer, confirming that the smallest water cluster found experimentally is the water hexamer. The XP spectra revealed strong waterwater interactions upon water adsorption at ~ 90 K, suggesting multilayer adsorption at this temperature. While increasing the temperature up to ~ 170 K, the water-water interaction vanishes, reflecting the monolayer water on the ZnO. Annealing the sample to ~ 200 K leads to the complete desorption from the graphitic part of the ZnO [12], leaving the co-existing monolayer water and surface hydroxyl groups on the higher ZnO layer, which is not graphitic. At ~ 300 K, only the surface hydroxyl groups on the higher ZnO layer remains. Further increase of the temperature leads to complete desorption.

5.3 Growth of Cs on the Moiré Pattern of Graphitic ZnO

Having discussed the hydration of the ZnO, we turn to study the adsorption of the Cs on the ZnO. We investigate the adsorption and structure of Cs on the Ag(111)-supported ZnO and further compare it with water.

5.3.1 Superstructure of Cs on ZnO



Figure 26: Imaging of Cs/ZnO at different polarities: STM images at (a) positive and (b) negative polarities; scanning parameters: $I_t = 130$ pA, (146 ± 1) K, (a) $V_t = +1.5$ V, (b) $V_t = -1.5$ V.

Alkalis transfer almost an electron to the oxide, for instance, [29,34], suggesting a formation of $Cs^{\delta+}$ ions on the oxide surface. The $Cs^{\delta+}$ ions are displayed as round protrusions at both polarities. In contrast, the moiré pattern of ZnO is visible only at the positive polarity (Fig. 26). Through our investigation, different polarities affect only the imaging structures of the moiré-patterned ultrathin ZnO film, but do not affect the $Cs^{\delta+}$ ions on it.

After understanding the effect on different polarities in STM imaging, we further investigate the dimension of the $Cs^{\delta+}$ ions on the ZnO. As we discussed previously (Fig. 26), the ZnO moiré pattern only appears at positive polarity. Here, the STM image is taken at a bias voltage of -1.5 V, so that the moiré pattern is not visible for easier interpretation. The $Cs^{\delta+}$ ions are imaged as round protrusions on ZnO with their diameters estimated by their FWHM (Fig. 27a). The diameter ranges from 1.12 nm to 1.63 nm with an average of (1.28 ± 0.09) nm (Fig. 27b). The apparent heights of the $Cs^{\delta+}$ ions are referred to the flat ZnO surface. The apparent heights vary from 116 pm to 165 pm with an average of (139 ± 16) pm (Fig. 27c). While using a bias voltage of +1.5 V, the apparent height of the $Cs^{\delta+}$ ions is then referenced to the protrusions of the ZnO moiré pattern, with an average



Figure 27: Dimension of the $Cs^{\delta+}$ ions on ZnO: (a) Height profile across these $Cs^{\delta+}$ ions along the orange line as marked in the inset at a unit cell coverage of $Cs^{\delta+}$ ions at 47%, (b,c) distribution of (b) diameter and (c) apparent height, $N_{tot} = 110$. (d) Height profile across a $Cs^{\delta+}$ ion along the orange line as marked in the inset at a unit cell coverage at 75% (e) distribution of apparent height, $N_{tot} = 26$. Scanning parameters: (a) $V_t = -1.5$ V, $I_t = 130$ pA, (146 ± 1) K, (b) $V_t = -1.5$ V, $I_t = 120$ pA, (146 ± 1) K.

of (53 ± 6) pm. Both distributions are rather narrow, further suggesting that single $Cs^{\delta+}$ ions are adsorbed on the ZnO surface.

After confirming the formation of the $Cs^{\delta+}$ ions on the ZnO surface, we turn to the coverage dependence of the $Cs^{\delta+}$ ions on the graphitic ZnO film. The $Cs^{\delta+}$ ions are imaged as well-separated circular protrusions (Fig. 28a). Small regions with a hexagonal pattern of $Cs^{\delta+}$ ions already form when only a third of the ZnO unit cells are occupied by $Cs^{\delta+}$ ions (unit cell coverage of 31%, orange circle in Fig. 28a). Further deposition enlarges these regions (e.g., at a Cs unit cell coverage of 72%, Fig. 28b), till a hexagonal superstructure forms at full unit cell coverage of 94% (Fig. 28c). The distance between the $Cs^{\delta+}$ ions in the hexagonal pattern and the superstructure is ~2.3 nm (orange bars in Fig. 28d), at all coverages, suggesting a $Cs^{\delta+}$ (1×1) superstructure on the ZnO moiré pattern. It contrasts with the coverage-dependent distance of $Cs^{\delta+}$ ions on metallic surfaces. For instance, the Cs–Cs distance in hexagonal superstructures on Cu(111) decreases from 1.1 nm at



Figure 28: Coverage dependence of $Cs^{\delta+}$ ions on ultrathin ZnO films: (a to c) STM images of $Cs^{\delta+}$ ions at unit cell coverages of (a) 31%, (b) 72%, and (c) 94% (d) Histogram of the next neighbor distance between $Cs^{\delta+}$ ions at a unit cell coverage of 94% on ZnO (orange bars) and water clusters at a coverage of 37% ML (blue bars, from Fig. 21b), $N_{tot}(Cs) = 204$, $N_{tot}(D_2O) = 145$. Scanning parameters: (a to c) $V_t = -1.5$ V, $I_t = 90$ pA to 160 pA, 140 K to 150 K.

coverage of 0.05 ML via 0.66 nm at 0.15 ML to 0.57 nm at 0.2 ML [28]. The distance results from a stabilization of the hexagonal superstructure through long-range adsorbate– adsorbate repulsion, indicative of the ionization of the Cs [28]. All Cs–Cs distances on Cu(111) [28] are significantly smaller than those of the Cs^{δ +} ions on the ultrathin ZnO film investigated here. The coincidence of the average distance of (2.3 ± 0.2) nm with that of the ZnO moiré pattern at all investigated coverages suggests that the adsorption of the Cs^{δ +} ions on the ZnO is rather governed by ion–surface interaction and not by ion– ion interaction. Compared to the D₂O clusters, the next neighbor distance of the D₂O clusters at 37% ML is also close to the periodicity of the ZnO moiré pattern of 2.3 nm (blue bars in Fig, 28d). The broader distance distribution of D₂O than that of Cs^{δ +} ions results from some unoccupied water adsorption regions of the ZnO moiré pattern at the highest coverage before coalescence. Thus, also the water distribution is governed by adsorbate-surface interaction.



Figure 29: Preferential adsorption sites on ZnO: STM images of (a) $Cs^{\delta+}$ ions (64%) on ZnO and (b) D₂O clusters (6% ML) on ZnO. Scanning parameters: $V_t = 1.5$ V, $I_t = 120$ pA, 145 K to 148 K.

Having discussed the strong adsorbate–surface interaction for both $Cs^{\delta+}$ ions and water clusters on the ZnO surface, we further investigate and compare the preferential adsorption regions of $Cs^{\delta+}$ ions and water clusters. The $Cs^{\delta+}$ ions are adsorbed onto the fcc regions (Fig. 29a). These fcc regions have the lowest LDOS on the ZnO moiré pattern, providing an energetically-preferred region (fcc in Fig. 17f). Note that the large size of a Cs atom of 343 pm in its van der Waals radius [66] as compared to the Zn–Zn distance of 328 pm in the ZnO layer suggests that it interacts with more than one surface atom. The Cs atom thus also interacts with three O atoms that encompass the Zn atom in this fcc region, distributing charge to the O atoms, forming a $Cs^{\delta+}$ ion. In contrast, the D₂O clusters nucleate in the electron-rich hcp regions of ZnO moiré pattern (Fig. 29b), as discussed in chapter 5.2.2.

5.3.2 Summary

After investigating the growth of Cs on the ZnO surface by STM, we summarize three points and compare them with the nucleation of water clusters on the same surface. First, while alkalis adsorb onto the oxide surfaces, they transfer almost an electron to the oxide, suggesting a formation of $Cs^{\delta+}$ ions on the oxide surface [29, 34]. The rather narrow distribution in the diameter and apparent height indicates a single $Cs^{\delta+}$ ion occupied in one protrusion, which also supports the formation of the $Cs^{\delta+}$ ions on the graphitic ZnO ultrathin film.

Second, the $Cs^{\delta+}$ ions form a (1×1) superstructure on ZnO at all investigated coverages with a next neighbor distance that matches the periodicity of the ZnO moiré pattern. The Cs–Cs distance is generally larger than that grown on Cu(111) [28], which is controlled by the repulsion between ions, implying an adsorbate–adsorbate interaction. In contrast to water and Cs^{δ +} ions adsorbed on the Ag(111)-supported ZnO, both adsorbates follow the periodicity of the ZnO moiré pattern, suggesting that both adsorption sites on the graphitic ZnO are governed by adsorbate–surface interaction.

Third, the preferential adsorption regions for $Cs^{\delta+}$ ions are at the lowest LDOS on the ZnO moiré pattern, i.e., fcc regions. The water clusters, however, nucleate at the electron-rich region on the ZnO moiré pattern, i.e., hcp regions. This difference is explained by the Cs atom distributing its charge to the electron-poor region, thus forming a $Cs^{\delta+}$ ion.

5.4 Hydration of Cs on the Moiré Pattern of Graphitic ZnO

Having characterized the two adsorbates separately, we now explore the influence of $Cs^{\delta+}$ ions on water nucleation and compare it with the nucleation of water on pristine graphitic ZnO. We discuss the formation of the one-dimensional chain structures on both pristine and $Cs^{\delta+}$ ion pre-covered ZnO with STM.

5.4.1 Hydration of the Cs Pre-Covered ZnO Moiré Pattern

Before discussing the hydration of the surface, we first clarify the definition of the D₂O coverage that is used in this chapter. Due to the comparison being only on the ZnO surface, here, the D₂O coverage is defined by STM and is as a percentage of the covered ZnO area. Thus, through this definition, the calculated numbers of D₂O coverages discussed here will be higher than in chapter 5.2. We investigate the influence of $Cs^{\delta+}$ ions on water nucleation at a D₂O coverage of ~32% ML at which the water clusters are well separated on the pristine ZnO film (blue arrows labeled "A" in Fig. 30a). Very few D₂O clusters on a neighboring hcp site coalesce at this coverage (blue arrow labeled "B" in Fig. 30a). This observation is quantified in a length histogram of the D₂O clusters normalized to the unit cell length of the ZnO moiré pattern of 2.3 nm. More than 95% of the D₂O clusters have the length of one unit cell, i.e., they occupy only one hcp site of the moiré pattern



Figure 30: Hydration of $Cs^{\delta+}$ ions on ZnO layer: (a, b) STM images of ~32% ML of D₂O adsorbed at (130 ± 5) K on (a) pristine ultrathin ZnO film and (b) ultrathin ZnO film pre-covered by 26% unit cell coverage of $Cs^{\delta+}$ ions. Blue arrows in (a) labeled "A" and "B" point to a D₂O cluster in a single hcp region and a D₂O cluster coalesced across two hcp regions, respectively. Green arrows in (b) labeled "C", "D", and "E" point to a linear, a 120°, and a 60° structure, respectively, white crossing lines refer to unit cell vectors connected through hcp regions of the ZnO moiré pattern. (c) Length distribution on hydrating the ZnO pre-covered with $Cs^{\delta+}$ ions (green) and pristine ZnO (blue) surface normalized to the unit cell length of the ZnO moiré pattern (2.3 nm), N_{tot}(Cs) = 53, N_{tot}(D₂O) = 85. Scanning parameters: (a) $V_t = 1.3$ V, $I_t = 90$ pA, (146 ± 1) K and (b) $V_t = 1.1$ V, $I_t = 70$ pA, (188 ± 2) K.

(blue bars in Fig. 30c). Only around 2.5% of the D₂O clusters connect two hcp sites, and another 2.5% more than two.

The hydration pattern of the ZnO pre-covered with $Cs^{\delta+}$ ions (26% unit cell coverage) at the same D₂O coverage is distinctly different. One-dimensional chains connect hcp regions; thus, they follow the unit cell vectors of the ZnO moiré pattern (green arrow labeled "C" in Fig. 30b). Larger one-dimensional D₂O-Cs chains exhibit distinct angles of 120° (green arrow labeled "D" in Fig. 30b) or 60° (green arrow labeled "E" in Fig. 30b). The clusters are substantially longer than on the pristine ZnO (green bars in Fig. 30c), with the clusters of length one reduced from 95% to 22%, and length two increased from 2.5% to 49%. Another 29% of the D₂O structures are longer than two unit cell. Thus, the presence of the $Cs^{\delta+}$ ions promotes the coalescence of water clusters between hcp regions.

5.4.2 Formation of the One-Dimensional Water Chain Structure

To understand the initial formation of the one-dimensional water-Cs chains, we co-adsorb smaller amounts of $Cs^{\delta+}$ ions and D_2O molecules. At a 26% unit cell coverage of $Cs^{\delta+}$ ions and 6% ML local coverage of D_2O , a D_2O cluster nucleates on an hcp region (blue arrow in Fig. 31a), elongated toward the fcc region (orange arrow in Fig. 31a). Furthermore, the formation of a one-dimensional structure is discovered at this low D_2O coverage (Fig. 31b). This structure has two D_2O clusters at hcp regions (blue arrows in Fig. 31b) connected via a protrusion in between (orange arrow in Fig. 31b). The angled structure is formed by two D_2O clusters at hcp regions (blue arrows in Fig. 31c) interconnecting through a protrusion near an fcc region (orange arrow in Fig. 31c). In comparison, these structures are not seen for D_2O at this coverage, suggesting an interaction of the $Cs^{\delta+}$ ion with D_2O



Figure 31: Initial nucleation of D₂O clusters on ZnO pre-covered with $Cs^{\delta+}$ ion: STM images of the water- $Cs^{\delta+}$ structures of (a) elongated cluster, (b) one-dimensional water- $Cs^{\delta+}$ chain, and (c) 60° structure. Scanning parameters: $V_t = 1.5$ V, $I_t = 80$ pA to 100 pA, (152 ± 2) K. Blue arrows mark the positions of the D₂O clusters nucleated on the hcp regions, orange arrows mark the extra protrusions which are not found upon the hydration of pristine ZnO surfaces.

molecules.

To further understand the inhomogeneous protrusions that are not observed after hydrating the pristine ZnO surfaces, we further analyze the structure by comparing their height profiles. Since the applied tunneling voltage highly influences the apparent height, we investigate every height profile with the same tunneling voltage of 1.5 V. The pristine D_2O clusters have different apparent heights while having different diameters. Here we demonstrate two D_2O clusters with one lower (Fig. 32a) and one higher (Fig. 32b) protrusion. Their height profiles range from 130 pm to 150 pm in reference to the protrusions of the ZnO moiré pattern (gray lines in Fig. 32f).

The height profiles for clusters in Fig. 31 are also measured and referenced to the protrusions of the ZnO moiré pattern. In the elongated cluster, the elongated part (orange arrow in Fig. 32c) is slightly higher than the smaller D₂O cluster (orange arrow points to the red line in Fig. 32f). Three protrusions appear in the height profile of the onedimensional D₂O-Cs^{δ +} structure (blue line in Fig. 32f). The apparent heights for two



Figure 32: Influence of $Cs^{\delta+}$ ions on height of D₂O clusters: STM images of (a, b) D₂O clusters on pristine ZnO, (c to e) D₂O clusters on ZnO pre-covered with $Cs^{\delta+}$ ions (f). Height profiles for (a to e) along the different color lines as marked in (a to e). Scanning parameters: $V_t = 1.5$ V, $I_t = 80$ pA to 180 pA, (150 ± 10) K. Arrows in different colors: yellow: hcp regions of the ZnO moiré pattern, orange: extra protrusions which are not found upon the hydration of pristine ZnO surfaces, blue: D₂O clusters.

of the protrusions at the hcp regions (blue arrows in Fig. 32d) are close to the apparent height of the larger D₂O cluster (light gray line in Fig. 32f), which is assigned to the D₂O clusters nucleated on the hcp regions. At the center of the linear structure, as well as the 60° structure, the centers exhibit a protrusion (orange arrow, Fig. 32d, e, and f). These features are not found in the hydration of the pristine ZnO surface, suggesting a different species on the ZnO moiré pattern. Considering the average apparent height of the Cs^{δ +} ions is (58 ± 6) pm (see chapter 5.3), the inhomogeneous protrusion is not the Cs^{δ +} ion, but the hydrated Cs^{δ +} ion. The apparent heights of these inhomogeneous protrusions are higher than the D₂O cluster and the Cs^{δ +} ion, further suggesting that the inhomogeneous protrusions are hydrated Cs^{δ +} ions. Furthermore, the positions of these protrusions are all at around X = 4 with a reference point at the hcp region of the ZnO moiré pattern, indicating a rather fixed adsorption position, i.e., near the fcc region, which further suggests the nucleation of D₂O molecules near the Cs^{δ +} ion on the fcc region.

5.4.3 Summary

After understanding the formation of one-dimensional water- $Cs^{\delta+}$ chains on the ZnO moiré pattern pre-covered with $Cs^{\delta+}$ ions, we discuss the difference between the formation of one-dimensional chain structures on pristine and $Cs^{\delta+}$ ion pre-covered ZnO surface. On the pristine ZnO surface, water clusters nucleate on the hcp regions of the ZnO moiré pattern at coverages below 85% ML, forming hexamers (chapter 5.2). Above 85% ML of water coverage on ZnO, the water clusters coalesce between hcp regions, forming onedimensional water chain structures. The presence of the $Cs^{\delta+}$ ions on the surface alters the nucleation of water clusters, the one-dimensional chain structures forming at a water coverage of $\sim 32\%$ ML. There are two types of water clusters that nucleate on the surface. One kind of water clusters nucleate at the position with the highest surface LDOS of the ZnO moiré pattern, which is the same as on pristine ZnO surfaces. Another kind of water clusters nucleates around a $Cs^{\delta+}$ ion, forming a hydrated $Cs^{\delta+}$ ion. The $Cs^{\delta+}$ ion interacts with water molecules that surrounded it, thus forming an inhomogeneous protrusion. This suggests that the $Cs^{\delta+}$ ions attract water molecules with their charge, thus, providing extra available nucleation regions on the surface. When these hydrated $Cs^{\delta+}$ ions grow larger by incorporating more water molecules into them, they connect to the existing water clusters on the hcp regions, forming elongated structures and further forming one-dimensional water-Cs chain structures. These one-dimensional water-Cs chain structures follow the unit vectors of the ZnO moiré pattern due to the connection between hcp regions. The increase in the available nucleation regions leads to larger water structures forming on the ZnO moiré pattern covered with $Cs^{\delta+}$ ions than on the pristine one. The presence of the $Cs^{\delta+}$ ions alters the adsorption behaviour and increases the

amount of water molecules in one region for reaction, thus offering a possible insight into how Cs promotes the water gas shift reaction on the Cu/ZnO catalyst.

6 Conclusion and Outlook

In this work, the growth of the graphitic ultrathin ZnO film on Ag(111) and the growth and distribution of the water clusters on the pristine and Cs pre-covered graphited ZnO are studied by density functional theory, low energy electron diffraction, photoemission spectroscopy, and variable temperature scanning tunneling microscopy.

The ultrathin ZnO film was successfully grown on the Ag(111) surface with physical vapor deposition and is monitored by photoemission spectroscopy. The Schockley-type surface state of the Ag(111) does not vanish after a full layer of ZnO cover on the Ag(111), instead, a new intermediate state is observed after deposition, indicating that there are still uncovered Ag(111) even at this coverage and the metallic property of the ultrathin oxide film. The structure of the ultrathin ZnO film was observed by low energy electron diffraction and scanning tunneling microscopy, their detailed structure was further confirmed with *ab initio* calculation. Ultrathin ZnO films have a structure of $ZnO(0001)-(7\times7)/Ag(111)-(8\times8)$ that exhibits a moiré pattern with a periodicity of ~2.3 nm, which comprises three regions, i.e., the hcp, the fcc, and the atop regions. This ultrathin ZnO film has a lattice constant of ~330 pm. Within the lateral precision of STM, the lattice constant of 325 pm is still in the range of the bulk ZnO(0001), indicating that the ultrathin oxide film retains its physical properties as the bulk material.

The structure and distribution of water clusters on Ag(111)-supported graphitic ZnO islands were investigated with variable temperature scanning tunneling microscopy and *ab initio* calculations. Multiple differences between the water clusters grown on ultrathin FeO films and ultrathin ZnO films were revealed. The ZnO moiré pattern confines the water clusters to its hcp regions. The highly-dispersed narrow-sized clusters present a favorable distribution of the water for further reactivity, e.g., in the water gas shift reaction. The pronounced higher cluster density at the border of the ZnO islands, regardless of the water coverage, suggests an upward mass transport of the water from the supporting metal to the oxide islands, increasing the water density at the catalytically active metal-oxide border.

The preference adsorption region for $Cs^{\delta+}$ ion on the ZnO moiré pattern, which is the fcc region, and the hydration of this surface were observed by scanning tunneling microscopy. The $Cs^{\delta+}$ ions form a (1×1) superstructure on the moiré pattern of ZnO with a separation of ~2.3 nm, indicating a strong adsorbate-surface interaction, which is the same as the water nucleation on the ZnO. The charge from the $Cs^{\delta+}$ ions attracts water molecules nucleating around it, forming hydrated $Cs^{\delta+}$ ions. The hydrated $Cs^{\delta+}$ ion attaches to the existing water hexamers on the hcp regions leading to the formation of the onedimensional water-Cs chain structure. This one-dimensional water-Cs chain structure has a local higher amount of water molecules due to the surface consist more available nucleating regions than on the pristine ZnO surface, increasing the water molecules in one region for reaction, thus offering an insight into the Cs-promoted water gas shift reaction in heterogeneous catalysis.

Our model system study by using a well-defined ultrathin ZnO film as oxide support reveals the first step of the adsorption and nucleation of water clusters on the pristine and $Cs^{\delta+}$ ion pre-covered surface in the heterogeneous catalysis, which assists future research on the first step of the water adsorption and nucleation in reactions including water as one of its reactants in heterogeneous catalysis. Also, we expect that the results in the hydration pattern influenced by the $Cs^{\delta+}$ ion are expected to be easily extended to the other alkali-based ions on their hydration in the heterogeneous catalysis.

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Acknowledgment

During the past six years, which I spent for my doctorate study in Germany, I was collaborated and supported by many people. The first person for whom I am very grateful is definitely my supervisor, Prof. Dr. Karina Morgenstern. Thanks for her support, especially in the interpretation of the data and the polishing of English. Thanks also to Dr. Alexander Birkner, who acts as the second supervisor of my entire study. He gave me plenty of useful discussions to enrich my content. Thanks to Prof. Dr. Talat Rahman and Dr. Duy Le from the University of Central Florida, who helps me to perform the calculation as well as many useful discussions to optimize and enrich both my thesis and two articles published in international journals.

I would further like to acknowledge Dr. Tianluo Pan, Dr. Christina Schunke, Dr. Cord Bertram, Dr. Karsten Lucht, Dr. Abijit Bera, Dr. Yunjun Cao, Dr. Sandra Metych, Dr. David Olivnza León, Marvin Quack, Kastur Meyer auf der Heide, Irene Weber, Prashant Srivastava, Vladimir Lykov, Iheb Baklouti, Inga Langguth, and other group members in the Physikalische Chemie I for their help in my daily life as well as many useful discussion and more, you are my best friends. I especially thank Dr. Niklas Osterloh and his family, who helped me a lot with the first step in Germany and to deal with my stay in Germany. The research will not able to proceed without having the instrument running. I also thank our permanent staff in Physikalische Chemie I, Mr. Volker Ader, Mr. Reiner Krause, Mrs. Gabriele Weitermeyer, Mrs. Jennifer Haag, Mr. Gerrit Niemeyer, Mrs. Ursula Ulde, and Mrs. Pia Hey for both technical and administrative support. Without your help, the lab will not run automatically!

Last but not least, I want to thank my family and my girlfriend in Taiwan for their encouragement as well as their mental support, without this, I could not stand to the end.