Stabilization of Polar ZnO Surfaces: Validating Microscopic Models by Using CO as a Probe Molecule

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The determination of the structure of inhomogeneous metal-oxide surfaces represents a formidable task. With the present study, we demonstrate that using the binding energy of a probe molecule, CO, is a reliable tool to validate structural models for such complex surfaces. Combining several types of first-principles calculations with advanced molecular beam methods, we are able to provide conclusive evidence that the polar O-terminated surface of ZnO is either reconstructed or hydrogen covered. This finding has important consequences for the ongoing discussion regarding the stabilization mechanism of the electrostatically unstable ("Tasker type 3") polar ZnO surfaces.

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Currently, there is a renewed interest in metal oxides including their surfaces, stemming in part from their relevance in various technological processes such as heterogeneous catalysis on an industrial scale. For ZnO, in particular, an additional stimulus comes from the more fundamental challenge to understand the stability of its two polar surfaces on a solid theoretical basis [1]. Briefly, polar surfaces of ionic crystals are electrostatically unstable and can exist only if the electric field generated by the nonzero projection of the dipole moment of the surface unit cell on the surface normal is compensated by an additional mechanism [2–4]. In the case of ZnO, the Zn-terminated (0001) surface (denoted here "Zn-ZnO") has to become less positively charged and the O-terminated $(000\bar{1})$ face ("O-ZnO") less negative by roughly a factor of 1/4 [5]. For various polar surfaces, several different stabilization mechanisms have been observed [6], including massive reconstructions [e.g., in NiO(111) and Cr_2O_3(0001)], loss of surface ions [e.g., in Cr_2O_3(0001) and Fe_2O_3(0001)], or the adsorption of charged species [e.g., in NiO(111)].

For the polar ZnO surfaces, however, several surface diffraction studies have failed to observe the presence of reconstructions. There is some evidence that the Zn-ZnO surface exhibits a high degree of disorder, since a random removal of 1/4 of the surface atoms was necessary to improve fits of gracing incidence x-ray diffraction (GIXD) data [7]. For the O-ZnO surface, however, no evidence for substantial amounts of surface vacancies was found in GIXD [1,7] and low energy alkali ion scattering [8]. In order to explain this apparent absence of the most common stabilization mechanisms for the case of the polar ZnO surfaces, it was proposed very early [5] that a transfer of electrons between the Zn-ZnO and the O-ZnO surfaces of a crystal may lead to a stabilization. A charge compensation of the polar surfaces by a redistribution of the electrons leads to partially filled surface bands, a situation usually assumed for polar semiconductor surfaces [4]. Although recent density functional (DFT) calculations appear to support this mechanism for ZnO [1], for no other polar metal-oxide surface has such a charge transfer been seen before. Thus, various microscopic models are still being discussed very controversially (see Ref. [9] for details).

These controversies also manifest themselves in the lack of understanding molecule-surface interactions even for simple probe molecules, e.g., carbon monoxide. Surprisingly, in early photoemission experiments [10] and recent molecular beam studies [11], it was found that the binding energy of CO on various neutral and polar ZnO surfaces is essentially the same, although slightly different values for the binding energies were reported (50 kJ/mol vs 30 kJ/mol). These findings are completely inconsistent with the results of *ab initio* studies [12,13] and also with the chemical intuition that the O-ZnO surface should not give rise to appreciable chemisorption of CO, in contrast to the Zn-ZnO surface, where a modest chemisorption is expected.

A novel and crucial aspect was recently discovered in He-atom scattering (HAS) experiments [14]. It was observed that O-ZnO surfaces with a (1 × 1) HAS diffraction pattern are always hydrogen covered [15], whereas after a careful removal of the hydrogen a (1 × 3) structure is found. This is a very puzzling result, since in basically all previous work the existence of a clean, unreconstructed (1 × 1) O-ZnO surface has been assumed.

Resolving the current debate regarding the microscopic structure of polar ZnO surfaces is severely hampered by the fact that most experimental techniques, e.g., spectroscopic methods [10], yield results integrated over the whole surface area, thus superimposing data for

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defective and perfect areas. To overcome this difficulty, we propose a new joint experimental/theoretical approach to validate the different microscopic models for the polar ZnO surfaces by using CO as a probe molecule. Experimentally, we determine the binding energies of CO by using a sophisticated molecular beam technique sensitive to the perfectly ordered parts of the surface alone. These results are then compared with calculations of the binding energies for different surface models. To exclude any bias, the full spectrum of available state-of-the-art first-principles methods was used in a synergistic manner. Highly accurate wave function based quantum-chemical calculations were employed within finite and embedded cluster setups, whereas DFT was used for infinitely extended periodic slab calculations after having been validated based on cluster benchmarks.

Experiments were carried out using a high-resolution (both angle and energy) molecular beam apparatus [16]. The apparatus is equipped with the facilities for LEED, x-ray photoelectron spectroscopy (XPS), and thermal desorption spectroscopy (TDS). All surfaces were thoroughly characterized using XPS, LEED, and HAS. Atomic hydrogen was adsorbed by operating a hot tungsten filament in line of sight at a distance of 10 cm from the surface [17] in a 10^{-6} mbar ambient of dihydrogen. LEED was found to be largely insensitive to the presence of H atoms on the surface [17]. For He atoms, in contrast, the cross section of adsorbed H atoms is fairly large (10 Å^2 [18]), so HAS was used to monitor H-atom adsorption and to structurally characterize the H-atom adlayers. CO adsorption was carried out either by backfilling the UHV chamber or by using a molecular beam where 3% of CO were seeded in He.

For the comparison with the theoretical results (see below), the experimental binding energies of CO on the flat, structurally well defined *perfect* parts of the different ZnO surfaces are required. With conventional TDS, however, desorption can be determined only in an *integrated* fashion, i.e., the signal from disordered parts (defects, steps, O vacancies, etc.) cannot be distinguished from that related to the perfect parts. Since from the very low intensity of the He-atom specular peak we can deduce that only about 0.1% of the ZnO surfaces consists of flat terraces with diameters exceeding 50 Å, a straightforward application of TDS for these structurally rather inhomogeneous metal-oxide surfaces is not possible.

To overcome this serious limitation of conventional TDS, we have used a molecular beam method where the binding of CO on the flat terraces can be determined separately. To this end, the He reflectivity of the surface is detected as a function of surface temperature [19]. Desorption of CO from the flat terraces strongly increases the He-atom reflectivity. Disordered or defective surface regions have very small He reflectivities and, hence, their contribution can be neglected. Typical results for the He reflectivity vs surface temperature curves are shown in Fig. 1 for three different surfaces, clean (1 × 1) Zn-ZnO, H-saturated (1 × 1) O-ZnO, and reconstructed (1 × 3) O-ZnO, saturated with CO. In all three cases CO desorption causes a pronounced increase in reflectivity. A quantitative analysis of the maxima of the first derivative (arrows in Fig. 1), which roughly correspond to the maxima in conventional TDS [19], yields CO-binding energies which are listed in Table I. For the H-saturated (1 × 1) Zn-ZnO surface [17] *no adsorption* of CO could be detected even at surface temperatures as low as 50 K, yielding an upper limit of the CO-binding energy of around 10 kJ/mol.

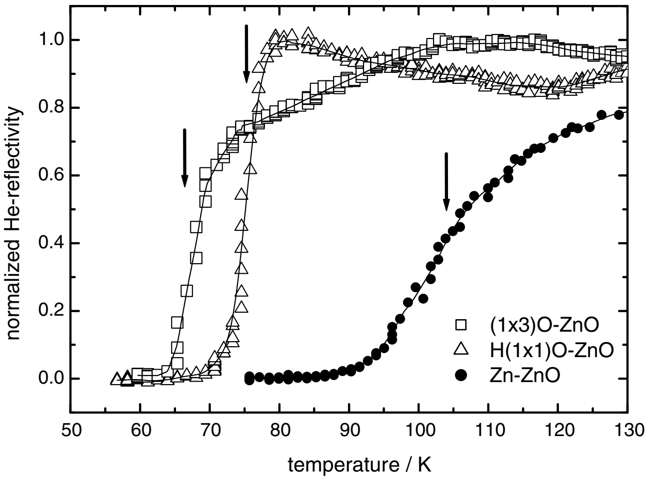

FIG. 1. Normalized He reflectivity vs surface temperature curves for CO adsorbed on clean (1 × 1) Zn-ZnO (filled circles), H-saturated (1 × 1) O-ZnO (open triangles), and reconstructed (1 × 3) O-ZnO (open squares) surfaces. The arrows indicate the maxima of the first derivatives.

In the theoretical part of the study, extensive *ab initio* calculations of the CO-binding energies were performed

TABLE I. CO binding energies (kJ/mol) on different polar faces of ZnO. "rep" indicates a pure repulsive interaction between CO and the corresponding surface. The experimental binding energy has been assumed to be equal to the activation energy for desorption.

	Expt.	Zn_4O_4 HF	Zn_4O_4 MC-CEPA	Zn_4O_4 DFT	$Zn_{13}O_{13}$ HF	Periodic DFT
			Zn-ZnO			
(1 × 1)	26.9	20.3	31.4	51.7	18.4[a]	36.2
H-sat	rep	rep		rep		rep
			O-ZnO			
(1 × 3)	17.0				13.7[b]	
(1 × 1)		1.0	2.4	rep	3.5	<2.0
H-sat	19.2	10.2[c]	12.0	14.0	18.6[a]	18.8

[a] Embedded cluster.

[b] Defect model for the (1 × 3) superstructure.

[c] At the HF level, the approach of CO in the "O-down" configuration is more favorable than in the "C-down" one; the binding energy for "C-down" is only 5.8 kJ/mol.

based on four different models for the clean and H-covered polar surfaces (see Fig. 2 for an overview). The first series of calculations was based on a free Zn_4O_4 cluster in a wurtzite-type structure [13]. This cluster was then enlarged to $Zn_{13}O_{13}$ and also embedded in a large array of point charges [20]. The Madelung field was constructed in such a way that fractional charges were added close to the surfaces—but not in the vicinity of the adsorption site—in order to compensate the large dipole moment of the isolated cluster (see Ref. [20] for details). Next, H atoms were added to the cluster surfaces in order to simulate the H-covered polar surfaces. Finally, for both the clean and the H-saturated Zn-ZnO and O-ZnO surfaces, periodic band structure calculations for a full CO monolayer coverage were performed using infinitely extended slabs with a thickness of eight Zn-O double layers [9].

The *ab initio* (embedded) cluster calculations were performed at Hartree-Fock (HF) and post Hartree-Fock levels [multiconfiguration coupled electrons approximation (MC-CEPA) [21]] with large extended basis sets of at least "TZ2P quality", i.e., triple zeta with two sets of polarization functions. All binding energies were counterpoise corrected [22] for the basis set superposition error (BSSE), which is mandatory for weakly bound systems. Selected cluster benchmarks, but, in particular, the large-scale periodic calculations with all atomic positions fully relaxed, were done with the semilocal Perdew-Burke-Ernzerhof (PBE) density functional [23]. Norm-conserving pseudopotentials were employed together with a mixed-basis set consisting of plane waves and localized, nonoverlapping orbitals for the O-2p and the Zn-3d electrons [9,24].

The results of the calculations are compared to experiment in Table I. Some caution should be taken when applying DFT to weakly bound systems. However, evidenced in Table I, the DFT calculations reproduce quite well the quantum-chemical data for the benchmark clusters, including electron correlation effects. In addition, they capture very nicely the trends in the CO-binding energies for the different cluster terminations. In particular, for the Zn-ZnO surface all calculations reproduce the experimental observation of a modest chemisorption of CO to the clean surface and a *purely repulsive* interaction if the surface is H saturated.

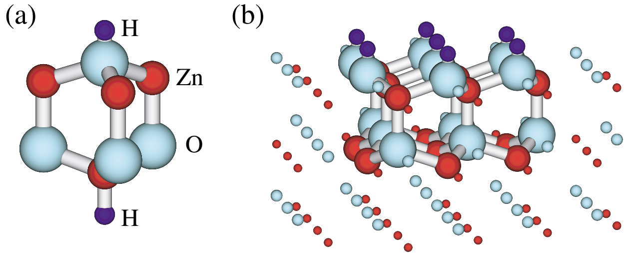

FIG. 2 (color online). Structures of the H-terminated (a) isolated Zn_4O_4 and (b) embedded $Zn_{13}O_{13}$ clusters using large spheres to represent the Zn, O, and H atoms as indicated and small spheres for the point charges. Note that the corresponding clean surfaces are obtained by removing the H atoms, that the isolated $Zn_{13}O_{13}$ cluster is obtained by omitting the point charges, and that the periodic slab corresponds to (b) after replacing the point charges by atoms (see text for further details).

The most important result reported in Table I is the fact that for the hypothetical clean (1 × 1) O-ZnO surface all theoretical models yield a binding energy for CO below 4 kJ/mol. This is significantly smaller than the experimental results reported in the literature [10,11] and also smaller than the new experimental value reported here for the hydrogen-free (1 × 3) O-ZnO surface. These results make the existence of an unreconstructed O-ZnO surface terminated by naked O atoms extremely unlikely. On the other hand, for the O-ZnO surface with an (1 × 1) hydrogen overlayer, both the DFT slab calculations as well as the calculations for clusters with OH groups yield binding energies of 10–20 kJ/mol. Such values are in very reasonable agreement with the experimental results reported here for the H-covered (1 × 1) O-ZnO surface, i.e., 19.2 kJ/mol. Moreover, our calculations indicate that the unreconstructed O-ZnO surface can energetically dissociate molecular hydrogen, lowering the energy by about 70 kJ/mol per H atom.

Finally, we consider a defect model which resembles the (1 × 3) reconstructed O-ZnO surface observed recently [14]. In this model, the $Zn_{13}O_{13}$ cluster was embedded in such a way that in the point charge field oxygen vacancies are mimicked by additional positive charges in the vicinity of the cluster itself. As in experiment, the CO-binding energy *decreases* relative to the unreconstructed but H-covered surface; see Table I. Note that the resulting binding energy is *not* very sensitive to the details in the positions and values of the additional charges, as long as charge neutrality and the compensation of the total dipole moment are preserved.

At first sight, the fact that the CO-binding energies for the H-saturated O-ZnO surfaces are significantly larger than for a hypothetical clean (1 × 1) O-ZnO surface is surprising. In order to unravel the microscopic origin for this unexpected difference and to understand why CO is bound to the clean Zn-ZnO surface but not to the O-ZnO surface, we have carried out a detailed quantum-chemical bonding analysis. To this purpose, we have applied the "constrained space orbital variation" analysis [25] to the adsorption of CO at the Zn_4O_4 clusters with and without hydrogen added to the cluster [see Fig. 2(a)]. The results of this analysis, performed at the HF level with inclusion of the BSSE correction, are collected in Table II.

One first realizes that there is a nearly complete cancellation between exchange (Pauli) repulsion and electrostatic attraction if CO approaches the Zn atom of the

TABLE II. Chemical bonding analysis of the interaction between CO and the Zn_4O_4 cluster (kJ/mol). ΔE_{elst} is the electrostatic interaction energy, ΔE_{XR} the exchange repulsion, and ΔE_{rel} the relaxation energy of the Zn_4O_4 cluster and the CO molecule, respectively. The four contributions add up to a value very close to ΔE_{HF}, the full HF interaction energy between Zn_4O_4 and CO. A fixed distance of 2.38 Å between the adsorption site of the cluster (O, Zn, or H atoms) and the C atom of CO was used.

Zn_4O_4 cluster	Clean		H covered	
	Zn-site	O-site	Zn-H	O-H
ΔE_{elst}	−72.1	−35.3	−2.7	−14.0
ΔE_{XR}	+77.0	+152.4	+24.7	+19.4
$\Delta E_{\mathrm{rel}}(Zn_4O_4)$	−5.0	−13.8	−2.4	−1.1
$\Delta E_{\mathrm{rel}}(\mathrm{CO})$	−18.3	−7.5	−1.9	−7.7
ΔE_{HF}	−19.9	+95.5	+17.9	−3.4

clean Zn_4O_4 cluster. Therefore, the bonding in this configuration is mainly caused by the electronic relaxation of CO (polarization of CO by the charge of the Zn ion and charge transfer from CO to the cluster). The approach of CO towards the O atoms, however, is repulsive because the exchange repulsion between the spatially much more extended O^{2-} ion and CO is much larger than all attractive contributions to the total interaction energy. A weak van der Waals attraction also does exist in this configuration, but it occurs at larger distances and has a binding energy of > 5 kJ/mol [13]. If the O atom gets hydroxylated by adding hydrogen, the exchange repulsion is greatly reduced since the electronic density of the OH^- group is mainly concentrated at the O atom. Now ΔE_{XR} is again largely compensated by the electrostatic attraction since the partially positively charged H atom can penetrate into the lone pair at the C atom of the CO molecule, and the bonding is mainly due to the electronic relaxation of CO itself.

In summary, our study demonstrates that by combining advanced molecular beam techniques and accurate first-principles calculations the adsorption of small molecules such as CO can actually be used as a probe to distinguish different microscopic models for even structurally rather inhomogeneous and complex metal-oxide surfaces. In our calculations we find significant differences between various models proposed for the two polar ZnO surfaces, and the origin of the different molecule-surface interactions is consistently explained in terms of a quantum-mechanical bonding analysis. In particular, our calculations predict unambiguously a pronounced difference between CO adsorption on the two clean, unreconstructed polar ZnO surfaces, namely, a *modest chemisorption* on the Zn-ZnO surface, but only a very *weak physisorption* on a (hypothetical) unreconstructed (1×1) O-ZnO surface. On the other hand, we find a significant adsorption energy for CO on the hydrogen-saturated O-ZnO surface. In comparison with the experimental findings, this clearly shows that the O-ZnO surface is either H covered or reconstructed. Altogether, our results *seriously* question the existence of a clean, unreconstructed (1×1) O-ZnO surface.

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