$c(2 \times 2)$ Water-Hydroxyl Layer on Cu(110): A Wetting Layer Stabilized by Bjerrum Defects

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(Received 11 November 2010; published 24 January 2011)

Understanding the composition and stability of mixed water-hydroxyl layers is a key step in describing wetting and how surfaces respond to redox processes. Here we show that, instead of forming a complete hydrogen bonding network, structures containing an excess of water over hydroxyl are stabilized on Cu (110) by forming a distorted hexagonal network of water-hydroxyl trimers containing Bjerrum defects. This arrangement maximizes the number of strong bonds formed by water donation to OH and provides uncoordinated OH groups able to hydrogen bond multilayer water and nucleate growth.

DOI: 10.1103/PhysRevLett.106.046103 PACS numbers: 68.43.Bc, 68.43.Fg, 71.15.Mb

On many wet oxide, semiconductor, and metal surfaces the first contact layer is not comprised of pure water but is instead a mixture of water and hydroxyl molecules, often caused by spontaneous dissociation of water. Although formation of water-hydroxyl wetting layers has been intensively investigated on well-defined metal surfaces [1], molecular-level understanding of this important class of overlayer is still far from complete and little is known about their local hydrogen bonding structure [2]. In particular, while it is established that hydroxyl coadsorption plays an important role in stabilizing water on metals [3–5], there is not yet a clear picture of the H bonding motifs adopted on different metals, nor how this changes the properties of the interface. For example, hydroxyl coadsorption can dramatically change the wetting behavior [6], while tuning the stability of adsorbed hydroxyl is key to optimizing the activity of surfaces for the oxygen reduction reaction [7]. Developing a detailed understanding of the coverage, bonding motifs and stability of hydroxyl underpins attempts to model electrochemical activity [8] and to develop a molecular picture of wetting [2–5,9].

The $c(2 \times 2)$ H_2O-OH phase formed on the open Cu (110) surface is one of the most widely studied model systems and affords an excellent opportunity to understand the structure and properties of this important class of overlayer. Water forms a number of unusual structures on this surface, including 1D chains of interlocking pentagons [10,11], an intact 2D network at higher coverage [10,12] and several partially dissociated structures [13–15], but the structure most commonly studied is the $c(2 \times 2)$ overlayer. Although it was originally believed that this corresponded to an intact water bilayer, more recent studies have shown that this is not the case and that it is instead comprised of a mixture of water and hydroxyl [12,13]. Whereas stoichiometric structures containing equal amounts of H_2O and hydroxyl have been observed on several metal surfaces, having each of the H atoms involved in 1 H bond and no uncoordinated OH groups [4], adsorption on Cu(110) [6] and Ru(0001) [5] results in a mixed phase containing an excess of water over hydroxyl. The excess of water is puzzling, since it provides too many OH bonds to form a complete H bonding network and may be in violation of the Bernal-Fowler-Pauling ice rules.

Here, we report an extensive series of experimental and theoretical studies of this system in which we show that nonstoichiometric structures are favored, having an approximate 2:1 H_2O-OH ratio. Formation of strong H bonds by water donation to hydroxyl leads to creation of novel $(H_2O)_2$-OH units. These units form the fundamental "building blocks" of the overlayer, the uncoordinated hydroxyl groups forming Bjerrum defects in which two H atoms sit between adjacent O atoms within a disordered hexagonal H_2O-OH network [16]. In contrast to fully H bonded stoichiometric H_2O-OH networks, which do not wet [17], Bjerrum defects in the $c(2 \times 2)$ layer on Cu (110) provide a source of uncoordinated OH groups, stabilizing multilayer adsorption [6,18].

The Cu(110) surface was prepared by Ar^+ ion sputtering, followed by annealing to 800 K. Scanning tunnelling microscopy (STM) images were recorded at 100 K in an ultra high vacuum STM (Specs 150) and supported by low energy electron diffraction (LEED) and temperature programmed desorption (TPD) to define the structures. Water dissociation is activated and H_2O-OH structures can be formed by adsorption at temperatures above 150 K [6], by electron damage [12], or by reaction with adsorbed O [12,19]. In this work H_2O-OH structures were formed by reaction of preadsorbed O (up to 0.1 ML) with different amounts of water at $100 < T < 140$ K. TPD measurements display the characteristic four-peak desorption spectrum reported previously [19].

As water is adsorbed onto the O precovered surface, STM images show the Cu-O chains disappear, being replaced first by hydroxyl dimers [15], and then by 1D structures parallel to $[1\bar{1}0]$ [14]. When the water coverage is increased further, islands of a distorted hexagonal $c(2 \times 2)$ structure appear, as shown in Fig. 1(a). This $c(2 \times 2)$ phase is invariably formed when excess water is coadsorbed with O at $T \leq 140$ K, irrespective of the exact coverage, and is also formed when an intact water layer is exposed to electrons [12]. The $c(2 \times 2)$ islands give sharp STM images, containing zig-zag chains that image above, or close to, the close-packed $[1\bar{1}0]$ Cu rows. Based on the initial coverage of O and the area of the surface covered by the $c(2 \times 2)$ phase, we estimate a composition of ca. $2\,H_2O$:1 OH, consistent with the ratio found recently by x-ray photoelectron spectroscopy (XPS) [6]. Although distinct contrast variations are observed at sites within the islands, no regular alternation in tunnel current is observed, such as might be anticipated for an ordered arrangement of hydroxyl and water. Increasing the water coverage further forms larger $c(2 \times 2)$ islands, but the abrupt changes in contrast disappear, Fig. 1(b), and clusters of second layer water appear, having an apparent height difference of ca. 1 Å to the first layer. This behavior is quite different to that of pure water layers at similar temperatures on Cu(110) [20], where STM images (not shown) find second layer clusters appear only once the first layer is complete. Since the $c(2 \times 2)$ phase is invariably observed when excess water is coadsorbed with O, or when an intact water layer is partially dissociated by electrons [12], it is clear the $c(2 \times 2)$ structure can stabilize further water at low temperatures, leading to the large and variable H_2O-OH ratio reported in earlier studies [13,19].

In order to explore possible structures associated with the $c(2 \times 2)$ phase, DFT calculations with the VASP code [21] were performed for a variety of pure water and water-hydroxyl overlayers. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [22] and the projector augmented-wave method was used [23], with a 415 eV cutoff for the plane-wave basis set and a Monkhorst-Pack [24] grid with at least $12 \times 12 \times 1$ k points sampling per 1×1 cell. Overlayers were adsorbed in a variety of unit cells, containing six Cu layers separated by a 14 Å vacuum gap. Atoms in the upper three metal layers and the water overlayer were allowed to relax until the forces were <0.025 eV/Å. Adsorption energies (E_{ads}) relative to gas phase water molecules were calculated by subtracting the total energy of the adsorbed water or water-hydroxyl overlayers from the total energies of the relaxed bare metal slab and isolated gas phase H_2O molecules. For the water-hydroxyl overlayers we assumed that the H atoms produced by water dissociation are chemisorbed on bare Cu. STM images were simulated using the Tersoff-Hamann approach [25].

The main results from the DFT calculations are summarized in Fig. 2 which plots E_{ads} for a range of water-hydroxyl overlayers. Results from more than 30 partially dissociated overlayers (PDOs) with different H bonding topologies and H_2O-OH ratios ranging from 1:1 to 3:1 are reported. There are several noteworthy features of these results. First, all the PDOs shown are more stable than any intact $c(2 \times 2)$ structures considered. Specifically, E_{ads} for the intact water structures discussed before [26] are only 545 meV/H_2O ("H-down" bilayer) to 489 meV/H_2O ("H-up" bilayer), whereas the PDOs typically have E_{ads} of >600 meV/H_2O. This result

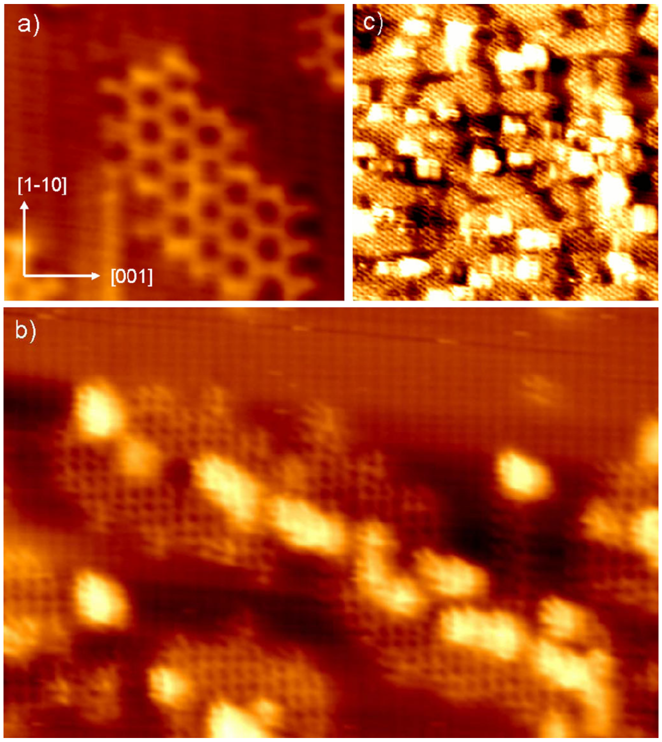

FIG. 1 (color online). STM images showing (a) island of the $c(2 \times 2)$ structure (44×38 Å^2) (b) increasing coverage with second layer growth (163×115 Å^2), (c) high coverage (300×300 Å^2). Growth temperature 140 K, imaged at 100 K, $I_t = -0.3$ nA, $V_t = -190$ mV.

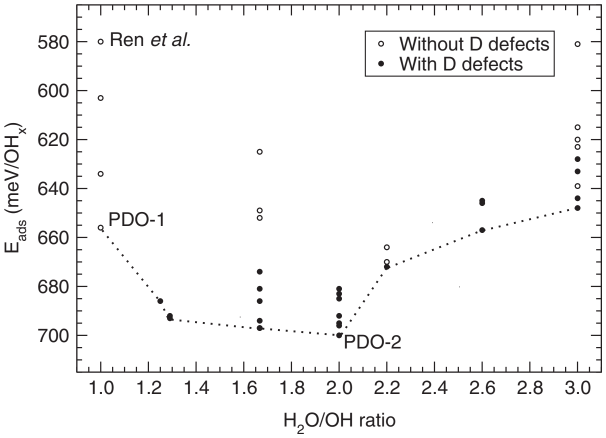

FIG. 2. Adsorption energy of different partially dissociated H_2O-OH structures on Cu(110). The most stable structure is PDO-2, shown in Fig. 3(c). PDO-1 is the most stable 1:1 H_2O-OH structure identified [Fig. 3(a)]. Ren *et al.* (Ref. [26]) indicates the most stable structure identified in previous work.

demonstrates that DFT-PBE correctly predicts that PDOs are favored over intact structures, as it does for water on Ru (0001) [5]. Second, the stability of the overlayers depends strongly on the H_2O-OH ratio, with structures containing an excess of water being favored. There is a broad shallow minimum in E_{ads} extending from about 1.3:1 to 2:1, with the most favorable composition being 2:1, consistent with the STM results and XPS [6]. The most stable 2:1 overlayer identified is about 45 meV/H_2O more stable than the best 1:1 overlayer and 120 meV/H_2O more stable than the PDO proposed previously [26,27]. Third, at each particular H_2O-OH ratio a range of structures with different stabilities are observed, indicating that the stability of the overlayer also depends sensitively on the H bonding arrangement.

Let us now consider the topology of the H bonding network within the overlayers. To begin it is useful to consider the most stable stoichiometric overlayer, comprising a 2D hexagonal H bonded network with water and hydroxyl molecules occupying atop sites, similar to the overlayers formed on close-packed metal surfaces [1]. The dipole moments of the molecules are inclined almost parallel to the surface so that every adsorbed OH_x species is involved in three H bonds (PDO-1, Fig. 3(a)]. STM simulations of the overlayer show that the hydroxyl groups appear much brighter than the H_2O molecules [Fig. 3(b)] and the resulting intensity alternation does not resemble the experimental STM image, supporting the conclusion that the $c(2 \times 2)$ structure is not a stoichiometric 1:1 overlayer. Structures containing excess water again have a quasihexagonal arrangement of molecules at atop sites and some of these overlayers also have continuous in plane H bonded networks, with some OH bonds in the excess water molecules pointing out of plane. However, surprisingly, the most stable structures all have defective H bonding networks containing Bjerrum *D*-type defects. This can be seen from Fig. 2 where, at all coverages considered, structures with *D* defects (filled circles) are more stable than structures without defects (open circles).

The most stable structure identified (PDO-2) is shown in Fig. 3(c) and has each hydroxyl group implicated in a *D* defect. Indeed we see from Fig. 3(c) that each *D* defect in this layer can be thought of as being constructed from two $(H_2O)_2$-OH trimers, where the hydroxyl group acts as an H bond acceptor to two H_2O molecules. Each H_2O molecule within the trimer can still form two further H bonds with other H_2O molecules, forming an extended hexagonal network. In fact, all the low energy structures found at other water-hydroxyl ratios also contain these trimer units, which represent the fundamental building block of the stable PDO-2 overlayer [Fig. 3(c)]. Essentially the system has sacrificed H bonds in which hydroxyl acts as a donor, so as to optimize the number of H bonds that hydroxyl groups accept, consistent with hydroxyl being a poor H donor but a good acceptor [2,6,28].

A simulated STM image of PDO-2 is shown in Fig. 3(d). The hydroxyl groups involved in the defect image brighter than the water molecules, while some of the H_2O donors attached to hydroxyl groups also gain intensity with respect to other H_2O molecules. Unlike the regular alternation in intensity predicted for the stoichiometric H_2O-OH network [Fig. 3(b)], this arrangement creates adjacent sites with high intensity. Experimental images of small $c(2 \times 2)$ islands, Fig. 1(a), do not show the regular alternation in intensity predicted for the stoichiometric structure [Fig. 3(a)], but instead display bright features at adjacent sites, similar to the features shown in Fig. 3(d). Unlike the regular array of *D* defects present in the simulation, a consequence of the unit cell chosen for the calculation, the bright features in the experimental images are disordered, suggesting a disordered array of *D* defects in these small islands. Since the overall $c(2 \times 2)$ O back bone is preserved, such H bond networks should be compatible with the observed LEED pattern. Compared to bulk ice, the O hexagons are expanded laterally by 13% along $[1\bar{1}0]$, while the STM images provide an estimate of 11 ± 3% for the average compression along [001], consistent with the ca. 13% predicted by DFT.

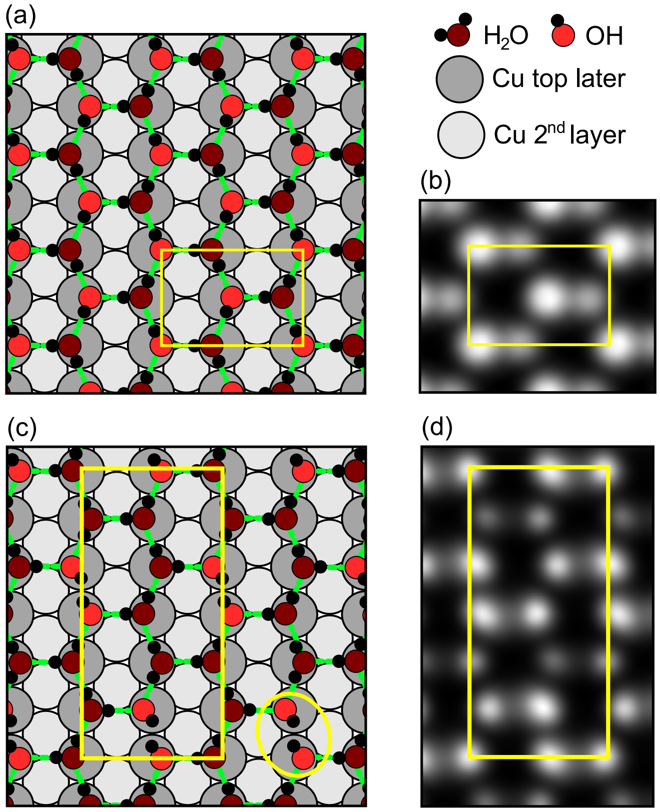

FIG. 3 (color online). Structures for (a) the stoichiometric $p(2 \times 2)$ PDO-1 and (c) $2\,H_2O$: 1 OH $p(2 \times 6)$ PDO-2 overlayers on Cu(110). Frames (b) and (d) show the corresponding STM simulated image (at 4 Å from the metal surface and $V = -200$ meV) for structures (a) and (c), respectively. PDO-2 (c),(d) is the most stable structure found, containing two *D* defects (yellow ellipse) in the unit cell (rectangle).

As well as explaining the excess of water over hydroxyl in the $c(2 \times 2)$ structure, the stabilization of Bjerrum defects offers new insight into the wetting behavior of this surface. Second layer water clusters form as hexagonal networks on top of the $c(2 \times 2)$ layer, Fig. 1(b), before the Cu surface is completely covered, whereas this is not observed for intact water layers [20]. Calculations show that adsorption of single H_2O molecules on top of PDO-2 takes place preferentially near D defect sites. Moreover, the adsorption energy of a single water on the structure rich in defects is 293 meV, 43 meV larger than that for water adsorption on the stoichiometric defect-free structure. Although these calculations are just for water monomers, they are consistent with the D defects playing a key role in multilayer growth and provide an explanation for the role of OH in stabilizing water multilayers on this surface [18]. In contrast, on stoichiometric structures (e.g., PDO-1) all the protons are involved in H bonds, with no OH groups free to bond to the second layer. Similar 1:1 H_2O-OH networks, formed on Pt(111), do not wet [17], so the observation that the $c(2 \times 2)$ structure on Cu(110) bonds effectively to further water is an additional indication the structure is different from the conventional stoichiometric layer suggested earlier [26].

Finally, we performed a series of DFT calculations to investigate why Cu(110) preferentially forms a nonstoichiometric overlayer containing $(H_2O)_2OH$ trimers, rather than the ordered 1:1 structures formed on other surfaces, such as Pt(111). Specifically, a 1:1 H_2O-OH overlayer (with a structure similar to [29]) and a 2:1 H_2O-OH overlayer containing one D defect were examined. This revealed that the 1:1 overlayer is marginally more stable on Pt(111) than the nonstoichiometric one, by 9 meV/H_2O, the opposite behavior to Cu(110) where nonstoichiometric overlayers are preferred by up to 45 meV/H_2O. In order to understand this we compared the most stable 2:1 structure for each metal surface; the average H bond length within the $(H_2O)_2$-OH trimers are 1.701 and 1.541 Å on Pt(111) and Cu(110), respectively, indicating that the trimer units are significantly more strongly H bonded on Cu(110) than on Pt(111). In addition, the computed binding energies of a single $(H_2O)_2$-OH trimer on Pt(111) and Cu(110) are 328 meV/H_2O and 567 meV/H_2O respectively, emphasizing the greater stability of the trimer unit responsible for stabilizing nonstoichiometric overlayers on Cu(110).

In summary, we have shown that the mixed H_2O-OH layer formed on Cu(110) is stabilized by formation of strong H bonds as water donates to hydroxyl, with nondonor hydroxyl groups accommodated as D-type Bjerrum defects. Previous studies have highlighted the crucial role of hydroxyl groups in stabilizing water adsorption at metal surfaces under near ambient conditions [18]; these results indicate that, unlike the fully H bonded structures formed on other surfaces, OH Bjerrum defects may play a crucial role as H donor sites in directing multilayer growth. Moreover, we demonstrate that maximizing the number of H bonds per molecule is not a reliable way to identify stable structures; the structure identified here contains fewer, but stronger H bonds than would be obtained with a traditional, perfect H bond network. The formation of D defects breaks the Bernal-Fowler-Pauling ice rules and permits the fraction of water and OH on the surface to vary continuously. Finally, the enhanced stability of the defective H_2O-OH layer on Cu(110) helps explain the reactivity of this particular surface to water dissociation [6], something that is reflected in its activity as a catalyst for the low temperature water gas shift reaction.

J. C. is supported by the Royal Society and is grateful to Matthias Scheffler for support. A. M's work is supported by the EURYI scheme, EPSRC, and ERC, A. H. by EPSRC and R. R. by EPSRC, BBSRC and EU.

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