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Hydrogen induced reconstruction of Cu(100): Two-dimensional and one-dimensional overlayers of surface hydride.

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Abstract

Adsorption of atomic hydrogen has a remarkable influence on the structure and morphology of the Cu(100) surface. We have examined two specific situations; the well-known reconstructed $p(2\times 2)$ -H surface and a one-dimensional (6×1) -H surface resembling the stripe reconstruction observed in an electrochemical environment. Electron energy loss spectroscopy and density functional calculations show that the H atoms occupy only surface sites and that H bonding in induced 3-fold Cu surface hollow sites is a structural key element. The calculations support a transient scenario in which H absorption in subsurface sites is a critical intermediate step in the reconstruction of the Cu surface. We find clear evidence in terms of characteristic properties, like the H-Cu bond lengths and the dipole excited vibrational mode spectra, that these structures consist of two-dimensional and one-dimensional overlayers of surface hydride.

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I. INTRODUCTION

Hydrogen adsorption on noble and transition metals surfaces is a key step in numerous catalytic reactions. Even though the catalyst, by definition, is not consumed in the process, the structure, morphology and chemical nature of the metal surface may be profoundly influenced by the adsorbed hydrogen. Recent *in situ* scanning tunneling microscopy (STM) measurements reveal a spectacular reconstruction of a Cu(100) electrode surface during the hydrogen evolution reaction [1]. At appropriate potential conditions the simple Cu(100) square lattice transforms, and stripes consisting of elevated rows of Cu atoms develop in a sudden transition. A similar one-dimensional reconstruction, resulting in long and defect-free single atom chains of Ir, has been observed using STM and low-energy electron diffraction (LEED) under ultra-high vacuum (UHV) conditions subsequent to hydrogen adsorption on the Ir(100) surface [2]. These reconstructions are induced by the adsorbed hydrogen but the STM and LEED measurements do not provide explicit information about the bonding of the hydrogen and its rôle in the process.

Regarding the Cu(100) surface, it is well established that adsorption of a monolayer of hydrogen atoms under UHV conditions has a profound influence on the structure and morphology [3–6] of the substrate surface, resulting in a reconstruction with displaced Cu atoms in an unusual p(2x2) structure. This structure has been found to be metastable and transform at substrate temperatures above 120 K [5]. Here we report surprising properties of the two-dimensional (2D) p(2x2)-H structure and its transformation into an unexpected one-dimensional (1D) (6x1)-H structure, which we believe is closely related to the stripe reconstruction of the Cu(100) electrode surface. We find, from electron energy loss spectroscopy (EELS) and density functional calculations (DFT), clear evidence in terms of vibrational spectra and H-Cu bond lengths that ordered 2D and 1D overlayers of surface hydride are basic elements in these surface structures. Decomposition of these compounds provides a reasonable explanation of the observed H₂ desorption kinetics [7] and the concomitant morphological changes of the pristine Cu(100) surface [1, 3, 5].

FIG. 1: LEED patterns of (a), the Cu(100) p(2x2)-H structure and (b), the Cu(100) (6x1)-H structure observed at 96eV and 57eV incident electron energy respectively.

II. EXPERIMENTAL

The Cu(100)-H structures, discussed in this work, were prepared in an UHV apparatus operating at a base pressure of 1×10^{-11} Torr. Atomic hydrogen species were produced by resonant electron induced dissociation of molecular hydrogen (H_2 , HD and D_2) physisorbed in a dense monolayer on the clean Cu(100) surface kept at a temperature of 10K [8, 9]. Electron induced desorption of the molecules was compensated for by an applied hydrogen background pressure in the 10^{-8} Torr range and dilution of the atomic species due to lateral diffusion was minimized by use of an extended electron beam spot pattern during the dissociation process [10]. Availability of adsorption sites as well as the recombination reaction [7] will result in a final saturation density of hydrogen atoms. Previous experiments [4, 5], using a calibrated nuclear reaction, show that the saturation density corresponds to one adsorbed atom per Cu surface atom. The atomic species will adsorb on the surface, but may also penetrate it and populate the subsurface and bulk region of the Cu specimen with a probability which depends on the specimen temperature and the kinetic energy of the incident hydrogen atoms [11].

In the present study LEED, EELS and work function measurements provide specific experimental information about the Cu(100)-H system at saturation density of H obtained at 10K and after brief annealings to temperatures in the range 80 K to 170 K. We know from our EELS measurements that the residual physisorbed hydrogen molecules desorb below 15 K and that only atomic species are observed above this temperature and that no hydrogen desorbs at the higher temperatures. The LEED patterns shown in Fig. 1 reflect the two characteristic structural situations we have encountered in the temperature range 10 K–170 K. The pattern in Fig. 1a, obtained after annealing to 80 K, corresponds to the reconstructed

Cu(100) p(2x2)-H structure of p4g symmetry reported in previous studies [3, 4]. We observe this structure even at 10 K, subsequent to the saturation dose of atomic hydrogen, which indicates that it forms with negligible thermal activation. The p(2x2) structure is known to be metastable and transform at higher temperatures [5]. A quick anneal from 60 K to 170 K results in a transformation into an unexpected 1D Cu(100) (6x1)-H structure shown in the LEED pattern in Fig. 1b [12], which we suppose is related to the stripe reconstruction of the Cu(100) electrode surface [1].

The change of surface structure and morphology is reflected in the work function change, $\Delta\phi$, with an increase relative to the clean well ordered Cu(100) surface by $\Delta\phi \sim +200\text{meV}$ and $\sim +300\text{meV}$ for the p(2x2)-H structure and the (6x1)-H structures, respectively. The change in surface morphology, subsequent to hydrogen desorption and a temperature increase to 450K, results in a work function decrease, $\Delta\phi \sim -100\text{meV}$, due to roughening of the clean Cu(100) surface [1, 3, 5]. Further details regarding the H-Cu bonding configurations and the structures are presented in Sections III, IV and V.

III. COMPUTATIONAL

Density functional theory is used in a real space grid [13, 14] implementation of the projector augmented wave method [15]. The calculations are performed with a grid spacing of 0.14 Å and the Perdew-Burke-Ernzerhof formula [16] is used to approximate the exchange and correlation contribution. Integration over the Brillouin zone is approximated by (8,8,1) Monkhorst-Pack sampling [17], and a temperature of 0.05 eV is used to smear the electronic Fermi distribution.

The Cu(100) surface is modeled in a p(2x2) computational cell with periodic boundary conditions in the x- and y-directions, whereas the z-direction is treated without periodic boundary conditions with a vacuum distance of at least 16 Å and the thickness of the surface is set to four atomic layers. The whole structure is relaxed until a convergence criterion of 0.01 eV/Å is met on the largest element of the gradients. Vibrational analysis is performed by finite differences within the harmonic approximation where IR intensities comes from a finite difference approximation of the gradient of the dipole moment [18]. The displacement used in the finite difference is 0.05 Å.

The two DFT structures shown in Fig. 2 refer to different initial conditions. Starting with

FIG. 2: Top view and side view of (a) the Cu(100) p(1x1)-H structure and (b) the reconstructed Cu(100) p(2x2)-H structure. The H coverage is one H atom (small sphere) per Cu surface atom (large sphere). Color code: Light brown Cu atoms and white H atoms.

H atoms in all 4-fold Cu hollow sites of the (2x2) supercell results in the p(1x1)-H structure in Fig. 2a with H atoms located in the 4-fold Cu hollow sites, 0.44 Å above the center of the Cu surface plane and with an H-Cu bondlength of 1.87 Å; in excellent agreement with the values 0.43 Å and 1.86 Å from a previous DFT calculation [19]. However, this structure is not observed in the experiments and it turns out that the p(1x1)-H structure is 0.09 eV less stable per supercell than the reconstructed p(2x2)-H surface shown in Fig. 2b, which has the same symmetry as the experimentally observed structure. This DFT structure results from an initial condition with 2 H atoms in 4-fold hollow sites and 2 H atoms in subsurface tetrahedral sites of the p(2x2) supercell. We note in this context that a population of subsurface H atoms was previously proposed as a possible cause of the observed reconstruction [4]. In the p(2x2)-H structure in Fig. 2b, the H atoms occupy only surface sites, 2 in 4-fold hollow sites and 2 in 3-fold hollow sites, which are located 0.01 Å and 0.86 Å above the center of the Cu surface layer with average H-Cu bondlengths of 1.77 Å and 1.78 Å, respectively. The Cu surface atoms are laterally displaced in such a way that contraction of every second Cu(100) square unit cell yields approximate hexagonal cells, resulting in the H bonding in energetically favourable 3-fold hollow sites. The structural parameters, vibrational mode energies and infrared activity of the p(1x1)-H and p(2x2)-H structures are given in Table I, and will be discussed in detail in the following sections.

We note that the initial condition given above is *sufficient* to produce the reconstructed p(2x2)-H surface. The importance of H bonding in the 3-fold hollow site was tested in

different ways. For example, if one of the 4-fold coordinated H-atoms is removed the reconstruction remains, or if an H atom in a 3-fold hollow site is removed one of the H atoms in the 4-fold sites moves to the 3-fold site and the reconstructed surface still contains 2 H atoms in 3-fold Cu hollow sites. We have also tested further initial conditions in the p(2x2) supercell, which resulted in three more local minima: (i) 2 H atoms in hollow sites and 2 H atoms in bridge sites, (ii) 2 H atoms in hollow sites, one H atom in a bridge site and one H atoms in a subsurface tetrahedral site, (iii) two H atoms in bridge sites and two H atoms in subsurface tetrahedral sites. The final structures are less stable by 0.15 eV, 0.39 eV and 1.05 eV per supercell than the reconstructed p(2x2)-H surface in Fig 2b.

TABLE I: Calculated structural and vibrational properties of the Cu(100) (1x1)-H and p(2x2)-H structures: $\bar{z}$ is the H atom position above the center of the Cu surface layer, $\bar{d}_{Cu-H}$ is the average H-Cu bond length in the 3-fold and 4-fold Cu hollow sites (the three nearest neighbour Cu atoms in the displaced 4-fold hollow site of the p(2x2)-H structure), $\omega^\perp$ and $\omega^\parallel$ are the energies of the perpendicular and parallel vibrational modes of H in these sites. I and $I^\perp$ are the total dipole active contribution and its projection along the surface normal to the intensity of these modes (the unit is $[(\frac{D}{\text{\AA}})^2 \text{amu}^{-1}]$)

	$\bar{z}$	$\bar{d}_{Cu-H}$	$\omega^\perp$	$\omega^\parallel$	$I_{\omega^\perp}$	$I_{\omega^\parallel}$	$I_{\omega^\perp}^\perp$	$I_{\omega^\parallel}^\perp$
	(\AA)	(\AA)	(meV)	(meV)				
<hr/>								
(1x1)-H								
4-fold hollow	0.44	1.87	68	88,90	0.421	0.007,0.002	0.421	0.000,0.000
<hr/>								
p(2x2)-H								
4-fold hollow	0.01	1.78	51	100,125	0.190	0.603,0.176	0.190	0.050,0.023
<hr/>								
3-fold hollow	0.86	1.77	117	95,127	0.322	0.034,0.227	0.320	0.003,0.017
<hr/>								

IV. THE p(2x2)-H STRUCTURE

The EELS spectra shown in Fig. 3 were obtained after a brief annealing to 80 K of the p(2x2)-H structure. All spectra reveal only atomic species, with prominent loss peaks at 56

meV and 117 meV and at 40 meV and 86 meV for the H and D atoms respectively, with characteristic isotope ratios close to the harmonic oscillator value $\sqrt{2}$. Fig. 4a shows the angular dependence of the loss intensities, I_n , for H together with predictions from EELS dipole scattering theory [20], which states that for a metal substrate, $I_n \propto |\mu_n^\perp|^2$, where $\mu_n^\perp$ is the component of the dynamic dipole moment along the surface normal for the vibrational mode n .

Plausible H-Cu bonding configurations can be inferred from the EELS data. As proposed in a previous study [3] we relate the 56meV loss peak in the H spectrum to H atoms occupying a 4-fold hollow site of the reconstructed surface. This vibration is excited via the dipole scattering mechanism as expected for the perpendicular motion of an atom adsorbed on a metal surface. The 117 meV loss peak is also dipole excited and is associated with a second H-Cu configuration. Different H sites have been proposed, either H *adsorbed* in a bridge bonded surface site as suggested from EELS observations [3] or H *absorbed* in a displaced tetrahedral site 0.9 Å below the Cu surface plane, with a short H-Cu bond length around 1.65 Å as proposed from ion scattering measurements [4]. Population of this subsurface site was also suggested to be the ultimate cause of the unexpected reconstruction of the H saturated Cu(100) surface [4].

The vibration transitions at 56 meV and 117 meV related to the two H sites are dipole excited, an expected observation for the perpendicular motion of an atom adsorbed on a metal surface. However, regarding dipole active vibrational motion of atoms absorbed in subsurface sites of a metal the expectation is different. The efficient screening due to the free metal electrons will result in negligible dipole activity of such species. This poses a dilemma regarding the proposed subsurface location of the second H site and the obvious conclusion from our EELS data seems to be that the H atoms populate a surface site.

Our DFT calculations shed light on this problem. In the lowest energy p(2x2)-H surface shown in Fig. 2b, the H atoms occupy only surface sites, 2 in approximate 4-fold hollow sites and 2 in approximate 3-fold hollow sites of the restructured Cu surface layer. The calculated intensities, $I^\perp$, of the dipole excited perpendicular and parallel vibrations of the H atoms are shown in Fig. 3 and provide, together with the corresponding EELS spectrum, crucial data for a conclusive test of the DFT structure. $I^\perp$, which is represented by a curve with a peak width of 9meV equal to the characteristic EELS peak width, shows the dipole contribution from these modes projected along the surface normal and hence fulfills the EELS dipole

FIG. 3: EELS spectra for the Cu(100) p(2x2)-H structure and its D and H+D counterparts measured at 60K in the specular direction for 3eV incident electrons. $I^\perp$ shows the perpendicular projection of the dipole active vibrational spectrum calculated for the DFT p(2x2)-H structure shown in Fig 2b. $I^\perp$ is represented by the characteristic EELS peak width of 9meV.

selection rule.

The intense peaks in $I^\perp$ at 51 meV and 117meV are due to the perpendicular vibration of H in the 4-fold and 3-fold hollow sites respectively, in very good agreement with the two prominent dipole excited loss peaks at 56meV and 117meV in the EELS spectrum. The parallel modes also contribute to $I^\perp$ resulting in peaks at 100meV and 125meV for the 4-fold site and at 95meV (weak) and 127meV for the 3-fold site. The splitting of these modes in two components is due to the non-symmetrical location of the H atoms in the two sites. These peaks are seen on the low- and high-energy side of the intense 117meV peak and they also appear in the broad dipole excited wings of the 117meV loss peak in the EELS

FIG. 4: Measured elastic and inelastic (x800) EELS peak intensities versus collection angle θ ($\theta = 0$ specular, $\theta < 0$ towards surface normal) for (a) the Cu(100) p(2x2)-H structure and (b) the Cu(100) (6x1)-H structure. The dashed curves show the EELS dipole scattering theory data adjusted to the intensity maxima of the inelastic angular distributions.

spectrum. Decomposition of this spectrum results in a central peak at 117meV and two surrounding peaks at 108meV and 126meV which we relate to the 100meV parallel mode of the 4-fold site and to a superposition of the 125meV and 127meV parallel modes of the 4-fold and 3-fold sites. We conclude from the very good agreement between the measured and calculated vibrational properties that the H atoms occupy the approximate 4-fold and 3-fold hollow sites of the restructured Cu surface shown in Fig. 2b.

The dipole active vibration modes observed in the spectra in Fig. 3 are due to the components, $\mu^\perp$, along the surface normal of the dynamic dipole moments of these modes. The total intensities, I , of the parallel modes, given in Table I, are in fact similar to the intensities of the perpendicular modes, which means that the corresponding dynamic dipole moments are of similar magnitude. This is a remarkable observation which shows that the Cu(100) p(2x2)-H structure is not a conventional adsorption system with H atoms chemisorbed on a metal surface; otherwise the free metal electrons would screen and cancel the dynamic dipole moments parallel to the metal surface.

A possible scenario, compatible with our observations, is that the restructured Cu-H surface layer is of non-metal character. Bulk CuH, a compound of the hexagonal wurtzite structure [21], is a semiconductor with a band gap around 0.6eV [22]. The broad infrared

absorption band [22], centered around 117meV, coincides with the energy 117meV of the dipole active vibration of H in the 3-fold hollow site of the p(2x2)-H structure. The H atoms have a tetrahedral surrounding of Cu atoms in CuH with an H-Cu bond length of 1.75Å. From the DFT structure in Fig. 2b, we have detailed knowledge about the location of the H atoms and the H-Cu bond lengths. In the 3-fold hollow sites the average H-Cu bond length is 1.77Å. The corresponding figure is 1.78Å for the H atoms relative to the three nearest-neighbour Cu atoms in the displaced 4-fold hollow site. These bond lengths are very close to the value for CuH and differ significantly from the bond length 1.87Å for H atoms chemisorbed in the 4-fold hollow site of the p(1x1)-H structure in Fig. 2a. We conclude that these observations support a model where the p(2x2)-H structure involves a 2D overlayer of surface hydride superimposed on the Cu(100) surface.

Regarding further structural details a comparison between the DFT structure in Fig. 2b and the ion scattering observations in Ref. [4] is of obvious interest. In the DFT structure, the H atoms occupy approximate 4-fold and 3-fold hollow sites located 0.01 Å and 0.86 Å above the center of the Cu surface layer. The Cu surface atoms are laterally displaced by ~ 0.44 Å in a pattern caused by contraction of every second of the Cu(100) square unit cells into approximate hexagonal cells resulting in H bonding in the critical 3-fold Cu hollow sites. The ion scattering data position H atoms in the 4-fold hollow site 0.35 Å above the Cu surface plane while the second site is located 0.9 Å below this plane in a displaced tetrahedral site. The measured lateral displacement of the Cu surface atoms and the p4g symmetry of the p(2x2) diffraction pattern permit the authors to propose a reconstruction of the first Cu layer in fair agreement with the DFT structure. Since the second H site also can be positioned 0.9 Å above the Cu plane[4], we find that the ion scattering data, and our spectroscopic and DFT data converge, in a compelling way, in the structure shown in Fig. 2b.

V. THE (6x1)-H STRUCTURE

The p(2x2)-H surface, which forms at 10 K is metastable and transforms around 170 K into a 1D (6x1)-H structure. From the LEED pattern in Fig. 1b, we know that the (6x1) unit cell is oriented in either of the two orthogonal [110] surface directions with cell edges equal to and 6 times the Cu(100) square unit edge, and the EELS spectra in Fig. 5 reveal

FIG. 5: EELS spectra for the Cu(100) (6x1)-H structures, and its D and H+D counterparts, measured at 60K in the specular direction for 3eV incident electrons. $I^\perp$ shows a tentative dipole active DFT spectrum with 2 H atoms in 4-fold hollow sites of the p(1x1)-H structure and 4 H atoms in the 3-fold hollow sites of the p(2x2)-H structure (the peaks at 95 meV and 127 meV are amplified by a factor of 5).

that specific changes of the H-Cu bonding occur, which provide support for a (6x1) unit cell with two distinct structural components. The 56 meV loss peak related to H-atoms in the 4-fold hollow site of the p(2x2)-H surface has shifted to 67 meV. We find that this vibration energy corresponds to H adsorption in the 4-fold hollow site on a regular Cu(100) surface, with a local p(1x1)-H arrangement. The DFT calculations for the (1x1)-H surface in Fig. 2a show that the perpendicular vibration energy of H in this site is 68 meV. Our EELS measurements at lower H coverages support this picture; the vibration energy for H adsorption in the 4-fold hollow site on the unreconstructed Cu(100) surface decreases from

73 meV to 70 meV when the H coverage increases from 0.1 to 0.5.

The high-energy range of the H-spectrum exhibits a particular feature; the loss peak at 117 meV, which appears at the same energy as the perpendicular vibration of H adsorbed in the 3-fold hollow site of the p(2x2)-H structure, is now quite narrow and split into distinct components at 103 meV, 117 meV and 129 meV as shown by the fitted line shapes in Fig. 5. Corresponding vibrational energies observed in the D-spectrum are 48 meV, 75 meV, 85 meV and 95 meV with H:D isotope ratios in the range 1.36 – 1.39 as expected for these species. The spectrum for HD establishes that only atomic species are involved and the angular measurements in Fig. 4b show that all the loss peaks in the H-spectrum in Fig. 5 are due to dipole excited vibrational transitions.

A tentative dipole active DFT spectrum for the (6x1)-H structure with 2 H atoms in the 4-fold hollow site of the p(1x1)-H structure and 4 H atoms in the 3-fold hollow site of the p(2x2)-H structure is shown in Fig. 5. The population of the two sites is chosen so that the relative intensities of the 68 meV and 117 meV perpendicular vibrations match the relative intensities of the 67 meV and 117 meV loss peaks in the corresponding EELS spectrum. We relate the peaks at 103 meV and 129 meV in this spectrum to the parallel modes at 95 meV and 127 meV of the 3-fold site in the $I^\perp$ spectrum. The degenerate parallel mode of the 4-fold site at 89 meV is not dipole active in the DFT spectrum and the lack of such a contribution apparently results in the distinct splitting of the perpendicular and parallel modes of the 3-fold site in the EELS spectrum. We note that the parallel modes are more intense in this spectrum than in the constructed $I^\perp$ spectrum. While $I^\perp$ refer to DFT data from two homogenous 2D structures, the EELS spectrum reflects the real inhomogenous surface with H atoms populating 3-fold hollow sites in a 1D arrangement which we, in analogy with the p(2x2)-H surface, suggest are stripes of surface hydride. We believe that the observed larger intensities of the parallel vibrations is a consequence of the specific properties of these protruding 1D structures.

Summing up our observations, we find that the (6x1) unit cell should contain H atoms adsorbed in 4-fold and 3-fold hollow sites, the former in a local (1x1) arrangement on an unreconstructed part of the unit cell and the latter on a reconstructed part. A one-dimensional structure composed of these elements is compatible with the stripe reconstruction of the Cu(100) electrode surface [1]. STM images show that stripes consisting of elevated approximately hexagonal rows of Cu atoms parallel to the dense Cu(100) atom rows develop, with

separations depending on the applied electrostatic potential. In the potential regime denoted $p(1 \times 8)$ the regions between the stripes consist of a regular Cu(100) square lattice. The reconstruction of the Cu(100) surface is induced by the adsorbed hydrogen. Our observations show that the H atoms occupy 4-fold hollow sites on the regular Cu(100) regions between the stripes and the characteristic 3-fold hollow sites on the hexagonal stripe regions, which we propose are 1D structures of surface hydride. A larger hydrogen uptake on the Cu(100) electrode surface results in an expansion of the surface layer by about 20% [1] which we believe is caused by H absorption in subsurface sites, presumably, resulting in a 2D layer of surface hydride.

VI. CONCLUSION

The DFT calculations and the experiments presented in this study give a fascinating picture of the hydrogen induced reconstruction of the Cu(100) surface. The calculations support a scenario in which absorption of hydrogen in subsurface sites is a critical intermediate step in formation of a reconstructed surface with the same symmetry as the experimentally observed Cu(100) $p(2 \times 2)$ -H structure. Our observations converge in a model of this structure with H atoms in 3-fold and 4-fold coordinated Cu hollow sites of a reconstructed surface layer. The Cu atoms are laterally displaced so that every second of the Cu(100) square unit cells contract into approximate hexagonal cells exposing energetically favourable 3-fold Cu hollow sites. We find that the structural and vibrational properties support a model where this surface layer is a 2D surface hydride superimposed on the Cu(100) substrate. The 2D $p(2 \times 2)$ -H surface transforms into a 1D (6×1) -H structure, which resembles the stripe reconstruction of the Cu(100) electrode surface during the hydrogen evolution reaction. Our observations indicate that the stripes are 1D structures of surface hydride separated by unreconstructed Cu(100) regions populated with chemisorbed H atoms in 4-fold Cu hollow sites.

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