



Hydrogen superstructures on Co nanoislands and Cu(111)

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ABSTRACT

Surface structures and related electronic properties of flat Co nanoislands supported on Cu(111) are studied before and after adsorbing different doses of molecular hydrogen at 10 K by low-temperature scanning tunneling microscopy/spectroscopy (STM/STS) at 5 K. It is found that the adsorption process on Co consists in two steps. First, H₂ dissociatively chemisorbs on Co forming an atomic H adlayer. Subsequently, molecules impinging on that H-terminated Co surface are physisorbed. When adsorbing a low dose of hydrogen on the Co/Cu(111) system, STM analysis shows that the chemisorbed hydrogen adlayer on Co forms a p(2 × 2) superstructure. On Cu surface however, no superstructure is observed. When adsorbing a high dose of H₂, hydrogen-induced superstructures are observed on both Co and Cu surfaces. These superstructures are ascribed to the presence of physisorbed molecules as revealed by the STS spectra. A (3 × 3) superstructure is observed on Co and a mixture of (2 × 2) and (3 × 3) is identified on Cu. A model describing the adsorption sites of molecules is proposed: H₂ molecules occupy on-top sites when arranged as a (2 × 2) phase and they occupy on-top and bridge sites when arranged as a (3 × 3) phase. Besides, STM-induced desorption is used to desorb atomic hydrogen from selected Co nanoisland surface. The desorption is visualized in terms of a disappearance of the p(2 × 2) superstructure.

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1. Introduction

Adsorption of hydrogen on transition metals was intensively studied in the past decades [1]. Motivations arose from the fields of embrittlement and heterogeneous catalysis. In order to reduce complexity and to understand the elementary steps of reactions, those studies were performed mostly on flat single-crystal surfaces. More recently, metal nanoparticles have attracted a lot of attention since it was shown that their catalytic properties differ from their bulk counterparts. These differences can be attributed to a high surface/volume ratio, changes in electronic properties due to size reduction [2], presence of surface irregularities as steps and kinks in the steps [3] and strains [4], all are known to strongly modify metal reactivity. Therefore, understanding of adsorption at the atomic scale of hydrogen on transition metal nanoparticles is of strong interest and might lead to the improvement of catalysts for hydrogenation reactions. In this paper, a scanning tunneling microscopy and spectroscopy (STM/STS) investigation of hydrogen adsorption at 10 K on Co nanoparticles and their Cu vicinity is presented. By submonolayer coverage, the Co/Cu(111) system provides perfectly flat, and strained Co nanoislands separated by areas of bare Cu(111) surface [5–7]. Since STM is a local imaging probe, it allows us to realize real-space observations at the atomic scale offering the most direct insight into the adsorption processes.

Although cobalt is an important transition metal in many catalytic reactions, experimental adsorption studies of hydrogen on that metal and particularly on single-crystal surfaces are scarce. Early UV photoemission experiments carried out on H-terminated Co(0001) surfaces showed that the presence of hydrogen quenches the *sp*-like surface state [8], highly attenuates the photoemission intensity, and slightly shifts the peak corresponding to the *d*-like surface state [9]. Adsorption on polycrystalline Co films showed that hydrogen chemisorbs dissociatively at $T_{\text{ads}} = 300$ K [10] and $T = 78$ K [11]. In their work, Duš and Lisowski identified two atomic chemisorbed forms and one molecular form occurring for high adsorption pressure. Bartholomew studied adsorption on supported Co nanoparticles on oxide substrates [12]. The main goal of these early studies was the determination of kinetics and energetics of hydrogen adsorption. However, no structural investigations describing the surface arrangement and the adsorption sites were performed. Only recently, Ernst et al. focused on the determination of hydrogen-induced superstructures and surface reconstruction on Co(10 $\bar{1}$ 0) by low energy electron diffraction (LEED) [13]. They observed four different structures depending on the hydrogen coverage. It was shown that for adsorption temperatures between 90 K and 200 K, hydrogen dissociatively chemisorbed on the Co surface and high-resolution electron energy loss spectroscopy revealed adsorption sites to be of threefold symmetry in all superstructures. Habermehl and coworkers showed that molecular deuterium dissociatively chemisorbs on Co(0001) between 180 K and 250 K and that

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adsorption results in a coverage saturating at 0.25 monolayers and corresponds to a (2×2) superstructure observed by LEED [14]. However, in this last study, the authors mentioned the fact that the LEED pattern was not reproducible probably due to damage caused by electron induced desorption. Contrary to cobalt, interaction of H_2 with Cu(111) is considered as a benchmark for activated adsorption [15]. At $T_{ads} = 78$ K, no adsorption is expected on Cu due to a high activation barrier. However, at $T \approx 10$ K, hydrogen molecules can physisorb on Cu(111) flat surface [16].

Recently, we also participated in this research by studying modifications of electronic properties of Co nanoislands epitaxially grown on Cu(111) induced by hydrogen adsorption and desorption from the surface of Co nanoislands at $T = 5$ K [17]. We showed that the hydrogen adsorption at $T \approx 10$ K quenches the *sp*-like surface state and the *d*-like surface state shifts downward in energy in agreement with UV photoemission performed on a Co(0001) single-crystal surface [8,9]. Most interestingly, we reported STM-induced desorption of hydrogen from the Co surface. We demonstrated that for bias voltages and tunneling currents beyond certain thresholds, it is possible to fully desorb atomic hydrogen from a Co nanoisland surface with tunneling electrons injected by a STM tip at $T = 5$ K. We showed that although the tip is immobile above the center of one island and thus the electron injection is point-like, the desorption occurs over a surface of several square nanometers. Nevertheless, the desorption is restricted to the surface of the island over which the tip is located. As the Co electronic properties depend strongly on the amount of hydrogen adsorbed, we showed that this cleaning effect creates the possibility to individually control the Co electronic properties island by island [17].

Given the state of the art of H_2 adsorption on Co, it is clear that, so far, no structural investigation was successfully performed on H-terminated Co(0001) surfaces. Accordingly, two fundamental questions remains unsolved: (i) What is the hydrogen arrangement on Co as a function of the coverage? (ii) What is the nature of the adsorbate on Co as a function of the coverage? Our goal in this paper is to give at least partial answers to those two fundamental open questions. We show different hydrogen-induced superstructures on Co and Cu surfaces as a function of the hydrogen coverage. Most importantly, we show that the nature of the adsorbate on Co, *i.e.* atomic or molecular, depends strongly on the coverage. Besides, we show that STM-induced desorption of hydrogen from Co surface can be visualized in terms of a disappearance of the hydrogen-induced superstructure.

2. Experimental details

The experiments were performed in an Omicron Ultra High Vacuum (UHV) system composed of three connected chambers: a preparation chamber for tip and sample cleaning treatments, a deposition chamber and a chamber with a low-temperature STM. The base pressure in the deposition and STM chambers was in the low 10^{-11} Torr range. The Cu(111) single-crystal was cleaned by repeated cycles of Ar^+ sputtering and annealing to 850 K. About half a monolayer (ML) of cobalt was evaporated with an electron beam evaporator at a rate of 0.1 ML per minute. During Co deposition at room temperature, the pressure in the chamber was about 5.0×10^{-11} Torr. After deposition, the sample was transferred as fast as possible (~ 5 min) to the STM chamber where the temperature is already kept at $T = 5$ K. Thus, the sample was immediately cooled down to prevent intermixing between Co and Cu. The temperature was measured by a regular silicon diode temperature sensor placed at 5 mm far from the sample. Typical duration of the measurements was 7–8 h. During that time, no degradation of

the sample was observed. We used polycrystalline W tips which were electrochemically etched *ex situ* and cleaned under UHV conditions by electron bombardment.

For spectroscopy, the tip was initially stabilized at a sample bias voltage U_s and a tunneling current I_s . The electronic feedback loop was then open. The differential conductance dI/dU was acquired via lock-in detection with a bias modulation of 10 mV at 4.8 kHz. Spectral curves on Co were measured with the tip located above the center of the island since it was shown that the electronic properties are strongly modified in the rim area [18]. Moreover, as electronic properties vary with the island size [19] and stacking [20], we discuss only STS spectra taken on islands of comparable sizes and stacking.

For adsorption experiments, hydrogen gas was introduced in the STM chamber by means of a high precision leak valve. During H_2 dosing, the sample was located in the STM chamber and a small aperture of 3×2 cm² allows hydrogen to condensate on the cold sample. This small open area led to an increase of temperature hardly controllable and depending on the opening duration. In our set of experiments, the adsorption temperature T_{ads} varied between 5 K and 10 K. The typical exposure duration was of the order of a few hundred seconds at a 10^{-7} Torr pressure. The exposures cited are in Langmuirs ($1 \text{ L} = 10^{-6}$ Torr s). As the hydrogen dosage is measured outside the cryogenic shields, the dosage actually reaching the cold sample can be roughly estimated to be at least 20 times lower taking into account the geometry of the STM chamber.

All STM images shown in the present work are current images. Although the tunneling current is set to a constant value to obtain topography images, small variations of the current can be induced by the surface structure and a finite time response of the feedback loop. Those variations give a so-called “current” image that is also representative of the surface structure. STM images were processed using WSxM software [21]. Regarding the reproducibility of our data, STS spectra and surface structures presented here were obtained several times with more than three different tips.

3. Clean Co nanoislands on Cu(111)

Prior to adsorption, verification of the cleanliness of the sample is realized. The Co nanoislands show a typical size of 10–30 nm and

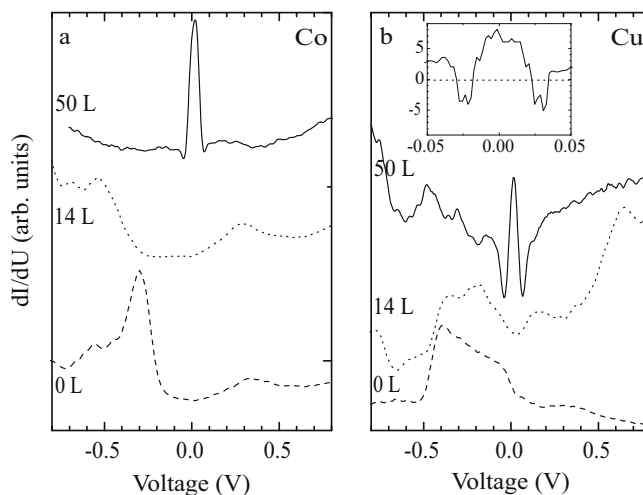


Fig. 1. Dependence of Co and Cu surface electronic properties on H_2 dose. dI/dU spectra obtained on (a) Co and (b) Cu surfaces after H_2 exposure at $T \approx 10$ K of 0 L (dashed line), 14 L (dotted line) and 50 L (line) ($I_s = 2$ nA, $U_s = -0.2$ V). The curves are shifted vertically for clarity. Inset of (b) shows a high-resolution dI/dU spectrum obtained on Cu at a dose of 50 L pointing out the negative differential conductance ($I_s = 2$ nA, $U_s = -0.8$ V).

a bilayer height as expected [5]. Two orientations are observed corresponding to two different stacking sequences [20,22,7]. All islands greater than 3–4 nm show the two well-known surface states, namely the minority *d*-like and the majority *sp*-like surface states [20,22,23]. First, a dI/dU spectrum taken on the Co surface before adsorption in Fig. 1a (plot labeled “0 L”) shows a sharp peak at -0.3 V corresponding to the localized *d*-like surface state. Second, a conductance map taken at positive bias voltage (not shown here) reveals standing wave patterns on Co resulting from the confinement of the Co *sp*-like surface state [20,22]. STS taken on the Cu substrate (see Fig. 1b, plot labeled “0 L”) shows a sudden rise of differential conductance at about -0.4 V which can be attributed to the onset of the Shockley surface state [24–26]. The presence of Co and Cu surface states is a clear evidence that the surface is uncontaminated.

4. H chemisorbed overlayer on Co

The sample is then submitted to a low dose (14 L) of hydrogen molecules at $T_{ads} \approx 10$ K. First, the surface structure of adsorbed hydrogen is investigated. Fig. 2a is a STM image acquired from Co and Cu(111) surfaces showing a surface structure solely on Co. Comparison between high-resolution STM images of the induced structure on Co in Fig. 2b and the clean Co surface lattice in Fig. 2c allows to determine a hydrogen-induced two-dimen-

sional hexagonal lattice not rotated with respect to the clean Co surface lattice, and characterized by a nearest-neighbor distance d_{NN} twice the one of clean Co, d_{CoNN} . The effective corrugation of the H-terminated Co surface is typically 12 ± 3 pm for a tunneling current of 1.9 nA and a bias voltage between -10 mV and -50 mV as shown in Fig. 2e.

Next, the nature of the hydrogen adsorbed at $T_{ads} \approx 10$ K on Co is addressed. In a complementary study, we observed that adsorbing a low dose of hydrogen at $T_{ads} = 78$ K again results in the formation of the same structure (not shown here) and the same electronic properties discussed below. As dissociation on Co is known to be not activated and as hydrogen dissociatively chemisorbs at $T_{ads} = 78$ K [11,14], it strongly suggests that this superstructure obtained at $T_{ads} \approx 10$ K is also induced by atomic hydrogen.

The determination of the atomic nature of the hydrogen allows us to deduce the adsorption sites. Indeed, according to density functional theory calculations, the most stable configuration for atomic hydrogen on Co(0001) is adsorption on threefold hollow sites [27]. Hollow sites form a honeycomb lattice as illustrated by triangles in Fig. 2d. The only superstructure formed by hollow sites, not rotated with respect to the Co lattice and showing a nearest-neighbor distance of twice d_{CoNN} is a $p(2 \times 2)$ illustrated as black dots in Fig. 2d.

In the following, the corresponding electronic properties of the hydrogen adlayer are determined by STS. In Fig. 1a, the main feature in the dI/dU spectrum of 14 L hydrogen-covered Co is a broad peak centered at -0.5 V. As already reported [17], this peak is assigned to the *d*-like surface state but shifted in energy from -0.3 eV for a clean Co surface to -0.5 eV for a H-terminated Co surface. For this specific dose, a $p(2 \times 2)$ superstructure is observed. However, observations of higher density superstructures are not excluded for higher doses. For example, it was shown that in most cases, a (1×1) superstructure is observed at saturation coverage of atomic hydrogen on fcc(111) surfaces [28–30].

Finally, the Cu surface is investigated. Although the Co surface exhibits an hydrogen overlayer, the Cu surface appears smooth and unchanged in Fig. 2a. The dI/dU spectrum labeled “14 L” taken over the Cu surface in Fig. 1b shows the Cu surface state as indicated by the step-like feature at about -0.4 V [24–26], therefore corroborating the absence of a hydrogen adlayer. These results suggest a hydrogen-free Cu surface.

5. STM-induced desorption

In a recent publication [17], we demonstrated that for bias voltages and tunneling currents reaching certain thresholds (0.4–0.5 V, 18 nA), it is possible to fully desorb atomic hydrogen from the surface of Co nanoislands with tunneling electrons injected by a STM tip at $T = 5$ K. The key feature of that process is the restricted area over which the cleaning is effective, corresponding to several nm², whereas earlier reported STM-induced desorption mechanisms are restricted to the atomic scale [31,32]. The desorption mechanisms are discussed in Ref. [17]. In that previous work, desorption by STM was indirectly detected in terms of changes in differential conductance. In the following section, however, we show that direct observation of desorption in real space is possible.

Fig. 3a shows a H-terminated Co(111) surface exhibiting a $p(2 \times 2)$ superstructure. The effective corrugation of that surface shown in Fig. 3e is typically 15 pm in agreement with results presented in the previous section. After injection of tunneling electrons into the Co characterized by current and voltage beyond the threshold values, two evidences suggest that hydrogen has been desorbed from the Co surface. First, the Co surface in Fig. 3b is homogeneous and smooth according to the cross-section profile

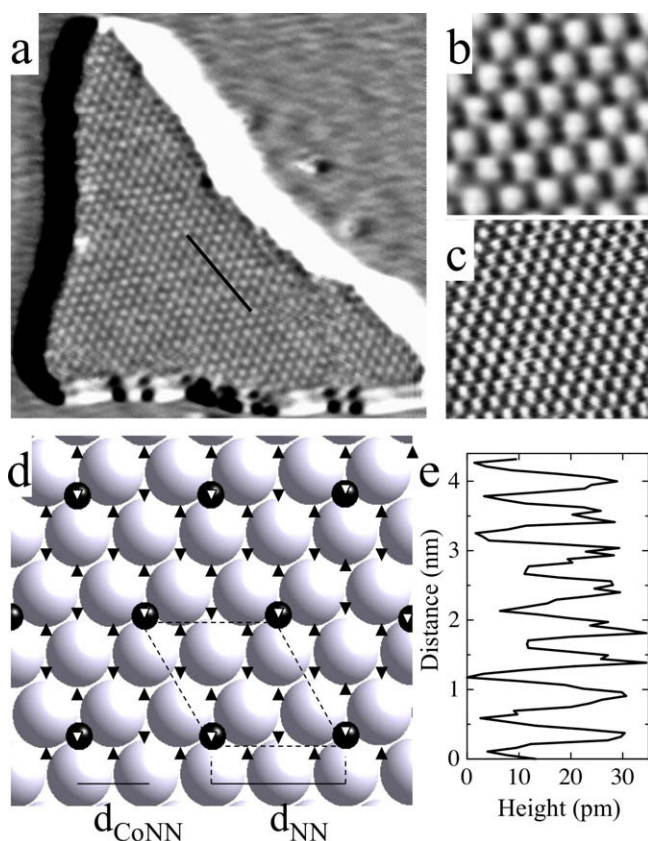


Fig. 2. Superstructure on Co induced by hydrogen adsorption at 10 K and the proposed atomic H arrangement. (a) 20×20 nm² STM image taken after adsorption at $T_{ads} \approx 10$ K of 14 L of H₂ ($T = 5$ K, $I = 1.9$ nA, $U = -0.050$ V). (b) 3×3 nm² zoomed region of hydrogen-induced superstructure in (a) ($T = 5$ K, $I = 1.9$ nA, $U = -0.050$ V). (c) 3×3 nm² STM image of clean Co ($T = 5$ K, $I = 160$ nA, $U = 0.009$ V). (d) Arrangement of hydrogen atoms in a $p(2 \times 2)$ structure on the honeycomb lattice formed by the threefold hollow sites of Co(111). Big white spheres are Co atoms. Triangles are threefold hollow sites. Black spheres are possible adsorption sites forming the $p(2 \times 2)$ superstructure. The dashed lines indicate the unit cell. (e) Cross-section profile along the black line in (a).

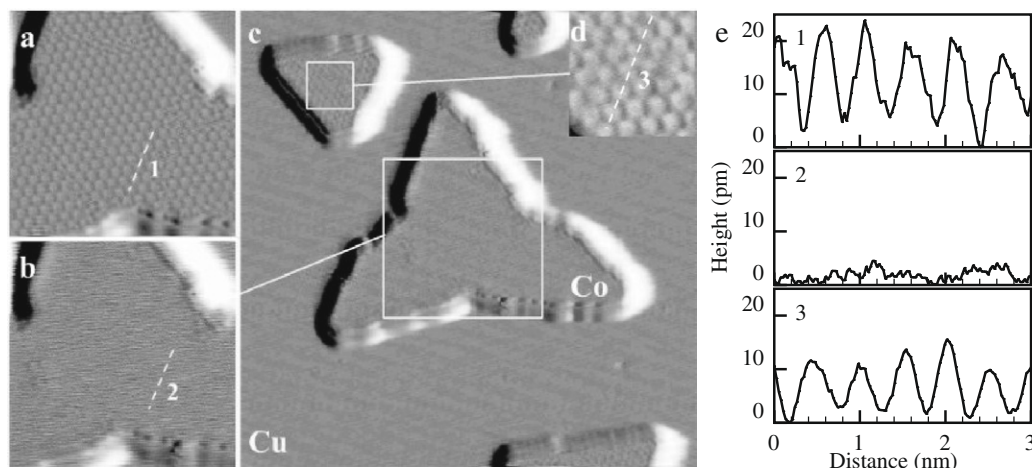


Fig. 3. STM-induced desorption of H from the Co surface. (a) $10 \times 10 \text{ nm}^2$ STM image showing the hydrogen-induced surface structure, taken after adsorption at $T \approx 10 \text{ K}$ of 14 L of H_2 . (b) Same area after desorption of surface hydrogen induced by tunneling current injected in the center of the nanoisland. (c) Larger area, $30 \times 30 \text{ nm}^2$, showing the entire island submitted to electron injection and its neighborhood. Note that the hydrogen-induced structure is still visible on the surface of surrounding island as shown by the (d) high-resolved $3 \times 3 \text{ nm}^2$ STM image taken over the top left island in (c). (e) Cross-section profiles along the white dashed lines labeled 1, 2, 3 in (a), (b), (d), respectively ($T = 5 \text{ K}$, $I = 1.9 \text{ nA}$, $U = -0.013 \text{ V}$).

taken on that island in Fig. 3e. Second, STS taken after injection reveals the surface has recovered its two surface states, namely the *d* and *sp*-like surface states.

The main feature of this process is that it is restricted to the surface area of the nanoisland exposed to injection in agreement with results obtained by the (*dI/dU*) mapping mode in our previous work [17]. Indeed, a zoom out of the Co surface in Fig. 3c reveals that the surface of the island submitted to electron injection is smooth whereas another island in the vicinity still exhibits a $p(2 \times 2)$ superstructure as illustrated by an atomically-resolved image in Fig. 3d and the cross-section profile both recorded on the surface of one neighbouring island. In conclusion, in combination with STS analysis of the *d*-like surface state, the desorption process of H from Co surface can be visualized in terms of a disappearance of the (2×2) superstructure.

6. H_2 physisorbed overlayers on Co and Cu

Higher exposures of hydrogen at $T_{\text{ads}} \approx 10 \text{ K}$ induce strong structural and electronic modifications for both Co and Cu surfaces. For exposure of 50 L, hydrogen-induced superstructures are observed on Co and Cu surfaces as illustrated in Fig. 4. Before describing these structures in detail, the nature of the adsorbed hydrogen is first addressed. Two evidences suggest that exposing the sample to a high dose of hydrogen at 10 K results in physisorption of hydrogen molecules on Co and Cu surfaces in contrast to atomic chemisorption on Co at low dose. First, as the desorption temperature gives indication for the chemisorbed or physisorbed nature of the adsorbate, after adsorption of 50 L of hydrogen at 10 K, we slightly increased the temperature up to 30 K. The sample was then cooled back to 5 K for analysis. At 30 K, we expect the weakly bound molecules to desorb contrary to chemisorbed atoms that are strongly bound to the metal and have accordingly a much higher desorption temperature closer to room temperature [8,10,14,15,33]. STM images and STS reveal that after heating up to 30 K, the Cu surface is smooth and clean whereas nanoislands exhibit an energy downshift of the *d*-like surface state, earlier attributed to atomic H adsorbed on Co. The second evidence of the physisorption of molecules on both metals is given by the STS in Fig. 1a and b taken after adsorption of 50 L of H_2 . This figure qualitatively shows two almost identical *dI/dU* spectra measured on Co and Cu. Regarding the Co spectrum in Fig. 1a, the spectral

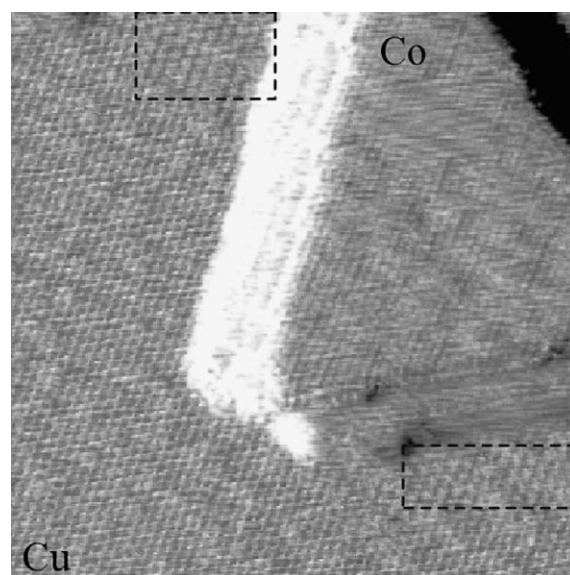


Fig. 4. Superstructures on Co and Cu submitted to 50 L H_2 at 10 K. $20 \times 20 \text{ nm}^2$ STM image ($T = 5 \text{ K}$, $I = 4.2 \text{ nA}$, $U = 0.019 \text{ V}$) shows that the surface exhibit a hexagonal lattice with a nearest-neighbor distance of 0.38 nm whereas rectangles illustrate regions of $p(2 \times 2)$ superstructure. The step-edges of the island are broadened due to a multiple tip.

feature related to the *d*-like surface state is vanished. The characteristic of both metallic surfaces is a pronounced peak centered at zero bias voltage with symmetric dips. In particular, the inset of Fig. 1b is a high-resolved (10 times smaller lock-in modulation) spectrum obtained on Cu with a high 50 L dose of hydrogen showing negative peak-like dips. This negative differential conductance has already been reported for H_2 on copper surfaces by STM [16] and more recently for H_2 molecular nanojunctions [34]. This spectrum can be described as two regions of constant conductance separated by sharp dips. This shape is the spectroscopic signature of H_2 molecules¹ [16,34]. The switching between a ground state and

¹ Although we observe in a systematic way this general shape, the observation of negative values of differential conductance depends strongly on the experimental conditions and detection parameters.

an excited state of the molecule of lower conductance is suggested to be responsible for the negative differential conductance. Therefore, the observation of such a spectrum is related to the presence of molecules on the surface.

The analysis of the electronic properties and the surface structures obtained for low and high hydrogen dose allow us to determine two adsorption steps: on the Co surface, dissociative chemisorption first occurs leading to the shift of the surface state until the formation of a monoatomic layer. Then, molecules can physisorb on the Co surface coated by chemisorbed H atoms. On the Cu surface, for short exposure time, the Cu surface state is not quenched probably due to a low sticking coefficient of H_2 at low temperature and low coverage [35]. For longer exposure, however, molecules physisorb on the Cu surface. This is in agreement with what is expected for Cu. Indeed, dissociation of molecular hydrogen on Cu(111) is an activated process as already mentioned above [15]. Accordingly, when exposed to molecular hydrogen, atomic hydrogen is not expected to be observed on the surface. However, it is likely to observe physisorbed molecules at very low temperature, typically below 20 K.

Next, the superstructures of molecular hydrogen adsorbed on Co and Cu are described and discussed. Independently of the metal, Co or Cu, Fig. 4 shows that molecules form a mixture of two kinds of ordered regions. The first one covers most of the surface, and is a two-dimensional hexagonal lattice with a nearest-neighbor distance d_{NN} of 0.38 nm that corresponds to 3/2 the nearest-neighbor distance of Cu (d_{CuNN}). The second one is an hexagonal lattice with

$d_{NN} = 2 \times d_{CuNN}$ corresponding to a $p(2 \times 2)$ superstructure shown on Cu in the dashed rectangles in Fig. 4. For the sake of clarity, it is important to note that although the surface arrangement in rectangles as a $p(2 \times 2)$ superstructure is similar to the one discussed in Section 4, we are here dealing with a molecular nature of the adsorbate.

Remarkably, the spacing 0.38 nm matches the bulk solid hydrogen lattice parameter [36]. Such specific spacing was already measured in Ref. [16] for physisorbed molecular adlayers on bare Cu(111) by STM. In that work, STM images revealed incommensurate ordered regions composed of a hexagonal lattice with a nearest-neighbor spacing of 0.38 nm. Moreover, those regions do not exhibit negative differential conductance features. Gupta et al. [16] deduced from their observations that the ordered regions are made of solid hydrogen. In the present case however, the hydrogen surface lattice is commensurate with the Cu(111) surface and negative differential conductance peaks are observed. Accordingly, no evidence suggests the formation of solid hydrogen in our case. Our STM analysis alone is not enough powerful to unambiguously identify the hydrogen state.

In the following, we show how further analysis of the magnified STM images allows us to determine the adsorption sites of the molecules on Cu. In Fig. 4, all molecules forming the hexagonal packing on Cu characterized by $d_{NN} = 0.38$ nm are imaged similarly. However, when changing the tip state, every second molecule appears brighter than the others leading to a more complex surface arrangement. This is shown in Fig. 5a where an enlarged fraction

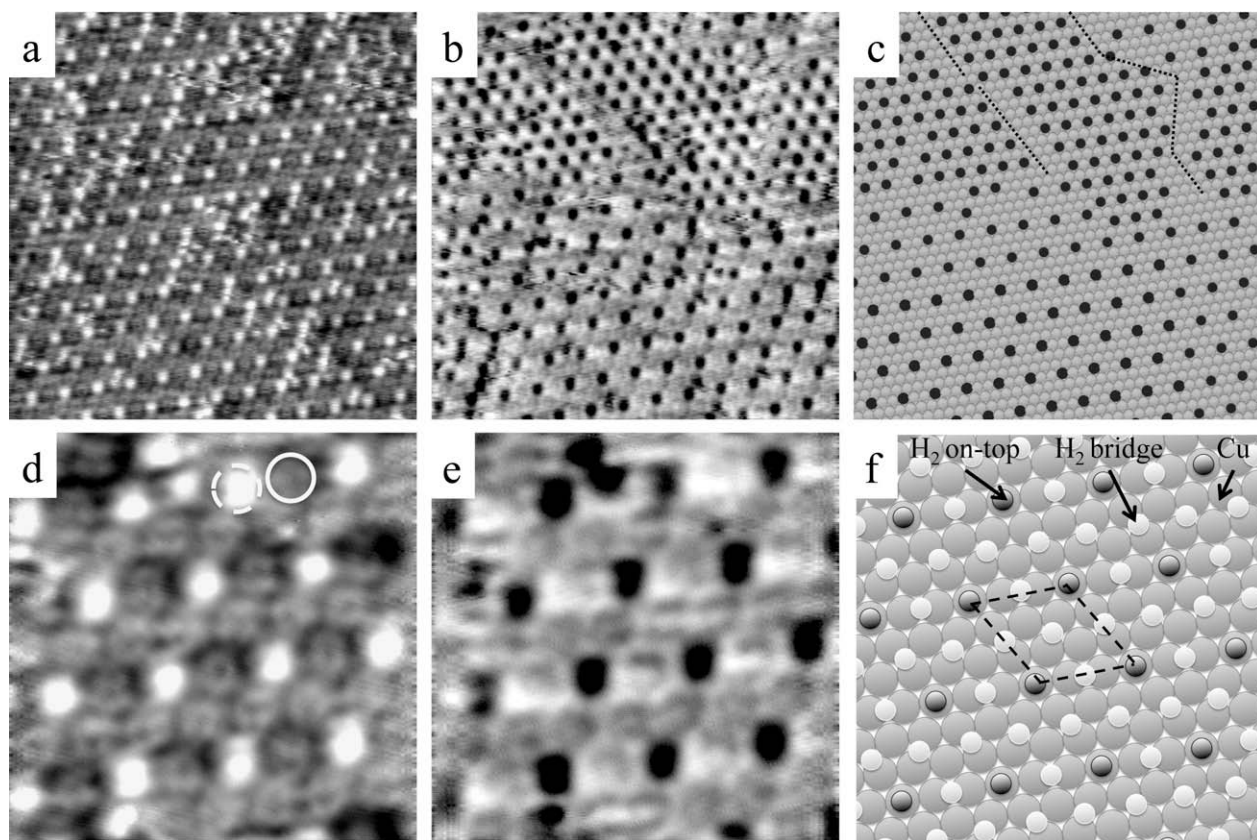


Fig. 5. Superstructures on the Cu surface of the 0.5 ML Co/Cu(111) sample being exposed to 50 L of H_2 at $T \approx 10$ K and molecular H_2 arrangements. (a) 10×10 nm² STM image showing a (3×3) superstructure ($T = 5$ K, $I = 9$ nA, $U = 0.028$ V). (b) 10×10 nm² STM image showing a mixture of (2×2) and (3×3) superstructures ($T = 5$ K, $I = 9$ nA, $U = -0.023$ V). (c) Structural model for H_2 molecules adsorbed on Cu(111). Light spheres represent Cu atoms. Dark spheres are H_2 molecules sitting on-top of Cu atoms. Molecules sitting on bridge sites (see text) are omitted for clarity. Dotted lines separate (2×2) domains (d and e) 3×3 nm² high-resolved STM images recorded simultaneously with positive (d) and negative (e) bias voltages showing details of the (3×3) superstructure ((d) $T = 5$ K, $I = 9$ nA, $U = 0.023$ V, (e) $T = 5$ K, $I = 9$ nA, $U = -0.023$ V). Circles in (d) distinguish two kinds of molecules. (f) Structural model showing the suggested sites for the Cu(111) – (3×3) superstructure. Big light spheres represent Cu atoms. Small dark spheres represent H_2 molecules sitting on-top of Cu atoms and small light spheres are molecules sitting on bridge sites. The dashed lines indicate the unit cell.

of the Cu surface in the vicinity of the Co island shown in Fig. 4 is taken after changing the tip state. It shows that instead of a homogeneous hexagonal lattice, the molecular overlayer is imaged as bright spots surrounded by a less intense background. Highly-resolved STM image in Fig. 5d show details of the surface structure for positive bias voltage. The pattern in the STM image of Fig. 5d can be described as bright spots indicated by a dashed line circle and less intense spots at half distance between two bright spots indicated by a full line circle. These two kinds of spots can be attributed to H_2 molecules adsorbed on different sites and therefore imaged differently by STM [37,38]. The hexagonal lattice formed by the bright spots in Fig. 5d shows a nearest-neighbor distance equal to $2 \times 0.38 = 0.76$ nm corresponding to about $3 \times d_{CuNN}$. The simplest scheme that could explain (i) a distance between molecules of $3/2 d_{CuNN}$ and (ii) adsorption on two kinds of sites, is given by molecules adsorbed on the on-top sites and on bridge sites at half distance between two on-top occupied sites. This is illustrated in Fig. 5f. In that adsorption configuration, molecules adsorbed at on-top sites are separated by $3 \times d_{CuNN}$ and the distance between molecules is $3/2 \times d_{CuNN}$. Molecules distributed on bridge sites are all electronically equivalent and thus imaged similarly by STM but differently than molecules at on-top sites. Molecules on-top of Cu atoms are identified as bright spots in Fig. 5d. Under these special imaging conditions, a (3×3) unit cell containing four H_2 molecules is thus observed. Another way to form a (3×3) hydrogen overlayer would be to consider adsorption on hollow sites. However, in that case, no site would be available at half distance between two hollow sites to host more molecules. Such a configuration can not explain our observations and is thus ruled out. In conclusion, the fine structure of the (3×3) seen in STM images strongly suggests adsorption of molecules on-top and on bridge positions. The orientation of the molecules and the interaction between them remain to be more completely understood, which, however, is extremely difficult from an analysis of STM images. In addition to those observations, we noticed that the contrast of the STM image in Fig. 5d is inverted when changing the sign of the bias voltage. This is illustrated by the STM image in Fig. 5e which was recorded simultaneously but with a positive bias voltage. In that figure, molecules adsorbed on-top sites are imaged darker than the surrounding molecules adsorbed on bridge sites.

Next, by analyzing Fig. 5b, illustrating the coexistence of the two $p(2 \times 2)$ and (3×3) surface arrangements, the adsorption sites for molecules forming the $p(2 \times 2)$ are determined. In Fig. 5b, the molecules forming these two surface arrangements are imaged similarly as black dots. We can argue that all molecules imaged as black dots sit on similar adsorption sites. In other words, the molecules of the $p(2 \times 2)$ are adsorbed on top of Cu atoms as well. Fig. 5c gives a clear illustration of the adsorption sites of the two structures namely (2×2) and (3×3) . Interestingly, the (2×2) superstructure exhibits 3 domains separated by dotted lines in the top of the STM image in Fig. 5b. Within the assumption that molecules forming the (2×2) sit on-top, the experimental image of Fig. 5b and in particular these three domains are perfectly reproduced in the scheme depicted in Fig. 5c. Finally, based on the fact that H_2 molecules physisorbed on Co adopt the same surface arrangement than on Cu as shown in Fig. 4, we can conclude that the adsorption configuration of the (3×3) obtained on Cu can be extrapolated to the H_2 overlayer adsorbed on the Co surface.

7. Conclusions

In this article, a scanning tunneling microscopy and spectroscopy investigation of hydrogen adsorption at 10 K on Co nanoparticles and their Cu vicinity is presented. First, prior to adsorption,

electronic properties of the Co islands and Cu(111) substrate are characterized. On both Co and Cu surfaces, STS reveals the presence of surface states, i.e. the majority *sp*-like and the minority *d*-like surface states of Co and the Cu Shockley surface state. These results demonstrate without any ambiguity that the Co and Cu surfaces are perfectly clean before adsorption. Second, the surface arrangement on Co as a function of the hydrogen dose is determined by analysis of STM images. We show that at low exposures, the Co surface exhibits a $p(2 \times 2)$ superstructure. Upon increasing H_2 exposures, a (3×3) superstructure is observed. In addition, the nature of the adsorbate as a function of the hydrogen dose is determined to be atomic for the first layer and molecular for high coverage. When the Co(111) surface is saturated with atomic hydrogen, molecular hydrogen physisorbs on the surface. The presence of the $p(2 \times 2)$ atomic overlayer is associated with an energy shift of the *d* surface state from -0.3 eV to -0.5 eV revealed by STS. At high hydrogen exposures, the Co surface shows a typical spectrum attributed to physisorption of molecules. Complementary, we study surface structures and related electronic properties induced by adsorption on Cu(111). Contrary to Co, the Cu surface remains unaffected when exposed to a low dose of hydrogen. However, upon increasing exposures, the *dI/dU* spectrum of Cu reveals negative differential conductance peaks attributed to presence of physisorbed molecules, similarly observed for Co. The Cu(111) surface exhibits a mixture of (2×2) and (3×3) superstructures. Models describing the adsorption sites of the molecules are proposed. STM images showing the dense (3×3) phase has been associated with molecules adsorbed on-top and on bridge sites, whereas molecules forming the (2×2) superstructure has been proposed to adsorb on-top sites only. Finally, we show that tunneling electrons injected from the STM tip into the Co surface of a nanoisland can induce full desorption of hydrogen atoms adsorbed on the Co surface. The desorption is visualized in terms of a disappearance of the $p(2 \times 2)$ superstructure.

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