

STM studies of ordered $(\sqrt{31} \times \sqrt{31})R9^\circ$ CO islands on Ag(111)

M. Kulawik,* H.-P. Rust, N. Nilius, M. Heyde, and H.-J. Freund

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

(Received 2 November 2004; published 25 April 2005)

The adsorption behavior of CO on Ag(111) is studied using low-temperature scanning tunneling microscopy. At submonolayer coverage, only single CO molecules are observed upon adsorption at 5 K. A further dosage leads to the formation of islands with various shapes and sizes. In addition, clusters with a diameter of about 11 Å are found that are mobile on the surface at 5 K. Though the position of the CO molecules within these clusters cannot be resolved, their size points to CO hexamers or heptamers. Well-ordered CO islands are observed only after heating the sample to 17 K, whereby two rotational domains with hexagonal $(\sqrt{31} \times \sqrt{31})R9^\circ$ structure are formed. A structural model is proposed in which CO hexamers represent the fundamental building blocks. The existence of two domains is explained with the alternate CO adsorption on the fcc and hcp places within the hexamers. The $(\sqrt{31} \times \sqrt{31})R9^\circ$ superlattice is the only well-ordered CO structure found in the temperature range between 5 K and 35 K.

DOI: 10.1103/PhysRevB.71.153405

PACS number(s): 68.37.Ef, 68.43.Hn

The interaction of carbon monoxide with transition metals has attracted much interest during the past decades. One reason is certainly the importance of CO in catalytically relevant processes, where transition metals often play a crucial role. Though the fundamental binding mechanism between CO and these substrates was described already in 1964,¹ the large number of recent experimental and theoretical investigations demonstrates the actuality of this subject.²⁻⁴ The central questions concern, for instance, binding sites, diffusion processes, and overlayer structures that are also important for the understanding of the CO-CO interaction.^{5,6}

Among the late-transition and noble-metal (111) surfaces, silver shows the weakest interaction with CO, with an adsorption energy of -0.28 eV.^{4,7} Therefore, the investigation of the CO adsorption on Ag(111) has proven to be very challenging. So far, studies have focused on CO-overlayer structures, which have been analyzed with a variety of techniques, such as angle-resolved ultraviolet photoemission spectroscopy (ARUPS), high-resolution electron-energy loss spectroscopy (HREELS), and low-energy electron diffraction (LEED).⁸⁻¹⁰ However, it has been difficult to unravel the structure, and indeed, a widely accepted structural model is still lacking. The main difficulty related to the above mentioned methods is their nonlocal nature, which means that they provide information averaged over all surface species. It is therefore difficult to distinguish between signals arising from a CO monolayer (ML) and signals from CO multilayers which are supposed to have different structures on Ag(111).^{9,10} Hence, knowledge of the exact adsorbate coverage is a crucial point for structure determination with nonlocal methods. This problem can be avoided using scanning tunneling microscopy (STM) which probes the local density of states of a surface and thus reflects its local electronic and topographic structure.

In the present study, STM is used to investigate the adsorption behavior of CO on Ag(111) for submonolayer coverages. In comparison with previous publications describing CO superstructures on Ag(111), the temperature range can be extended down to 5 K. At this temperature, we do not ob-

serve CO structures with long-range order, unless induced by interaction with the STM tip. Normally, disordered islands and small clusters are found, the latter containing probably six or seven CO molecules in a ringlike structure. A well-ordered CO superstructure, growing on Ag(111) in two domains, forms only at temperatures above 17 K. Based on the STM data, a structural model is suggested, differing from known CO superstructures, such as the herringbone or the pinwheel structure.

The experiments are performed with a home-built Eigler-style STM,¹¹ operated in ultra-high vacuum (UHV) at 5 K. The Ag(111) sample was cleaned by cycles of alternating Ar sputtering and annealing to 780 K. Figure 1(a) displays the surface topography after a dosage of CO at 5 K.¹² At this coverage, CO is adsorbed in the form of single molecules. These are imaged as depressions with a mean diameter of 6 Å, and they do not exhibit long-range order since their diffusion is suppressed at 5 K.¹³ In Fig. 1(b), the coverage is increased,¹³ and disordered CO islands (I) are formed as well as small CO clusters (II), imaged as 11 Å large, round pits. These CO clusters are characterized by their increased stability as compared to that of larger clusters, which are called

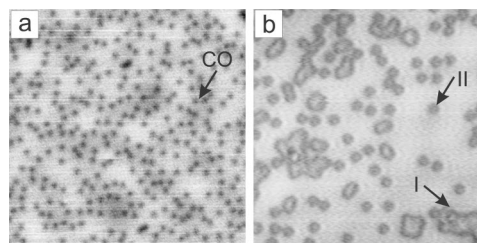


FIG. 1. (a) STM image of a Ag(111) surface after a dosage of CO at 5 K ($V_S=7$ mV, $I_T=3$ pA, $25\text{ nm} \times 25\text{ nm}$). CO adsorbs on the surface in the form of single molecules, imaged as black dots. (b) Disordered islands (I) and small clusters with a diameter of ~ 11 Å (II) form at a higher CO coverage ($V_S=20$ mV, $I_T=11$ pA, $25\text{ nm} \times 25\text{ nm}$). It is important to note that the original CO coverage was much higher. However, some of the clusters and islands were wiped off during the scan process.

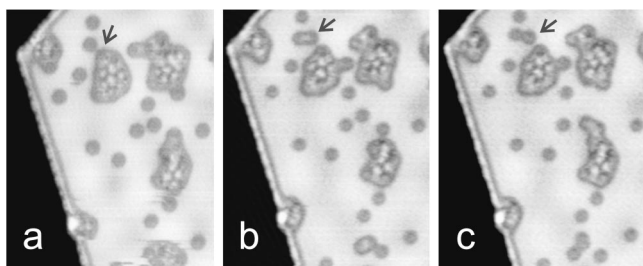


FIG. 2. Image series of small CO clusters and islands formed at 5 K ($V_S=5$ mV, $I_T=5$ pA, 16 nm \times 20 nm). The clusters are mobile at 5 K; they join and leave the CO islands (arrows), indicating their stability. The tip influences the cluster mobility and causes the ordering of some islands.

“disordered islands” in the following. Both the high internal stability and the mobility of the small CO clusters are revealed in the image series [Figs. 2(a)–2(c)]. The images show that these clusters can join and leave CO islands, underlining their exquisite size and properties. The structure of the small CO clusters cannot be deduced directly from the STM images, since the positions of the CO molecules are not resolved within the clusters. However, the round cluster shape, the diameter of 11 Å, and the substrate symmetry point to CO hexamers or heptamers. Similar structures are found, for instance, in bulk CO and in the so-called CO pinwheel structure on graphite.^{14,15} In both cases, the CO is orientationally ordered due to its quadrupole moment, whereby six in-plane-oriented CO molecules surround one normal-oriented CO. On the other hand, it is important to note that these heptamers are not isolated, but that each CO molecule is part of two pinwheels (heptamers). It is therefore difficult to transfer this structural model to the isolated clusters, and theoretical studies are needed to clarify this question. The phenomenon that special cluster sizes show an increased stability has been reported for various systems. Prominent examples include water on Pd(111) or 1-nitronaphthalene on Au(111).^{16,17} Sometimes the cluster formation is accompanied with an elevated mobility of the clusters as compared to the monomers.¹⁶ Such an effect was described for the CO chains on Cu(110), where dimers and trimers were found to diffuse faster than monomers.¹⁸ However, the stability of these chains did not depend on their length. To our knowledge, no characteristic cluster sizes have yet been reported for CO, for which the intermolecular interaction is much weaker than for the above mentioned systems. The CO clusters observed here are especially interesting, because they might constitute the “building blocks” of the ordered CO layers.

Most of these clusters disappear upon heating the sample to 17 K for 10 min, and well-ordered islands with hexagonal symmetry form on a purely thermodynamic pathway without the influence of the STM tip [Fig. 3(a)].¹⁹ Interestingly, two domains *A* and *B* can be distinguished, which are also visible in the corresponding power spectrum in Fig. 3(b). After a further dosage of CO at 5 K, small clusters are formed which frame the ordered islands as depicted in Fig. 3(c). Obviously, the CO clusters have to overcome a certain energy barrier to be integrated in the ordered islands. Further heating of the

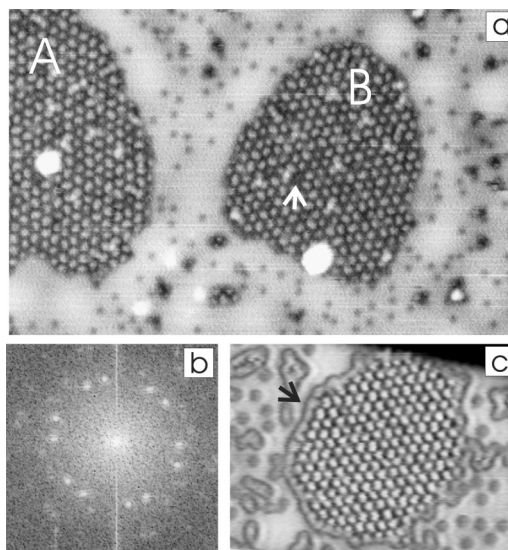


FIG. 3. (a) STM image of a Ag(111) surface after a dosage of CO at 5 K and 10 min heating to 17 K ($V_S=-10$ mV, $I_T=10$ pA, 40 nm \times 26 nm). In addition to the single CO molecules (dark points), well-ordered hexagonal CO islands are observed, which grow in two domains, *A* and *B*. Their orientation with respect to the Ag(111) lattice is shown in Fig. 4. The white arrow marks a “defect” where the building block of the island appears completely dark. (b) Power spectrum of (a), clearly reflecting the existence of two domains. (c) Well-ordered CO island with a fringe of small CO clusters ($V_S=20$ mV, $I_T=11$ pA, 23 nm \times 18 nm). Though the building blocks of the ordered island and the clusters have comparable sizes, the latter are not perfectly incorporated at 5 K.

sample up to 35 K and subsequent cooling to 5 K did not lead to other structures.

The analysis of the ordered islands shows that the two domains are rotated against each other by 18° , and by 21° with respect to the hexagonal Ag(111) lattice.²⁰ Figure 4(a) displays schematically the superstructure visible in the STM and the silver substrate. Apparently, CO forms a commensurate $(\sqrt{31} \times \sqrt{31})R9^\circ$ superlattice on Ag(111). The derived unit cells of the two domains are drawn in. As for the small clusters, the positions of the CO molecules within the $(\sqrt{31} \times \sqrt{31})R9^\circ$ superstructure cannot be extracted directly from the STM images. The lattice constant of 9.3 Å suggests that the protrusions forming the hexagonal lattice in the STM image do not reflect the positions of the CO molecules, since typical intermolecular distances in the CO adsorbate layers are in the range of 4 Å to 5 Å. Furthermore, single CO molecules are imaged as depressions on Ag(111), indicating that the dark outlines of the protrusions correspond to the CO molecules. The protrusions themselves might then be ascribed to places on the Ag(111) surface that are not covered with CO molecules. Thus, the possible building blocks of the ordered CO islands could be small CO rings with a size of about 9.3 Å. They might have a similar structure as that of the CO clusters observed at 5 K, with the exception that no CO sits in the middle of the ring. This model would also explain the observation of defects in the hexagonal superstructure where the building blocks appear completely dark [cf. Fig. 3(a)]. In this case, an additional CO molecule might

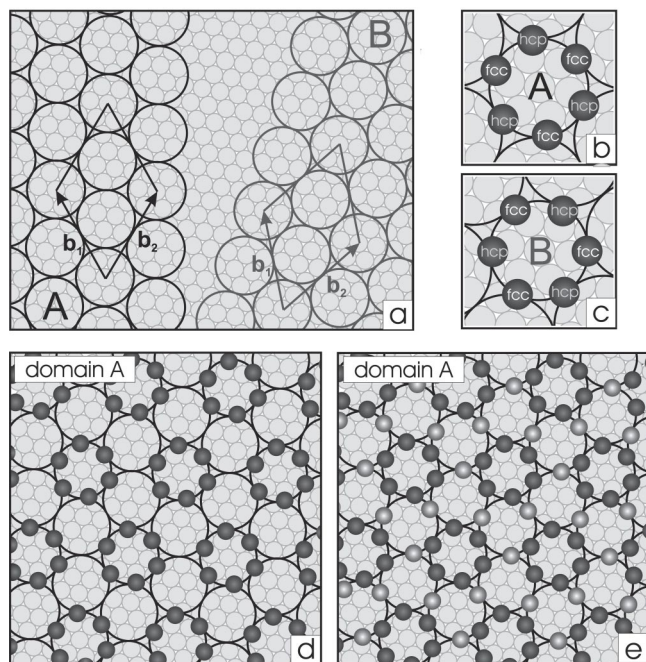


FIG. 4. (a) Scheme of the mapped superstructures *A* and *B* (large circles) with respect to the underlying Ag(111) lattice (small circles). The structure visible in the STM corresponds to a commensurate $(\sqrt{31} \times \sqrt{31})R9^\circ$ superlattice. (b) and (c) Structural model, in which the building blocks of the ordered islands consist of CO hexamers (dark bullets). Two domains *A* and *B* would result from the alternate occupation of the hcp and fcc sites. (d) and (e) Possible arrangements of the CO hexamers for the *A* domain. Whereas in (d) the islands consist exclusively of CO hexamers, additional CO molecules (bright bullets) are inserted in between in model (e).

be adsorbed in the center of the ring. The slight size difference (9.3 Å compared to 11 Å) might be due to different imaging properties in the STM of islands and isolated clusters.

A central question concerns the origin of the two rotational domains of the superlattice. Taking up the model of the CO rings, one explanation would be that CO molecules occupy, alternately, the fcc and hcp sites of the Ag(111) substrate as illustrated in Figs. 4(b) and 4(c). Here, the CO molecules are represented by dark bullets, while the CO superstructure visible in the STM is reflected by black circles. The scheme shows that such CO hexamers would indeed lead to two differently oriented domains *A* and *B*, which are rotated against each other by 18° . Based on this model, several structures are conceivable, two of which are proposed in Figs. 4(d) and 4(e) for the *A* domain. In model (d), the CO superstructure is built of hexamers, whereby each CO is part of only one hexamer. As a result, the area between the two hexamers would have a lower CO coverage, and one might therefore expect that two different units of the superlattice would be discernible in the STM. However, this could not be observed, and so the structural model (e) seems to reflect the STM image in a better way. Here, CO molecules are suggested to occupy additional sites between the hexamers. This model takes into account both the stability of the CO clusters observed at 5 K and the energy barrier of

~ 17 K for the island formation. This temperature could then be interpreted as the energy necessary to partly break and rearrange the CO rings, which would also explain the observation of hexagonal islands framed by CO clusters [Fig. 3(c)].

Though this model agrees very well with our experimental results, it is questionable whether CO adsorbs in threefold hollow sites on Ag(111). So far, only the on-top adsorption of CO on Ag(111) has been experimentally proven. This finding is based on HREELS studies, revealing a CO stretching frequency of 266 meV, which is typical for an on-top adsorption.⁹ However, the CO is only weakly adsorbed on Ag(111) with an adsorption energy of -0.28 eV,⁷ and recent density functional theory calculations suggest that the adsorption energy for different sites is almost degenerate on Ag(111).⁴ Furthermore, the adsorption site can depend on the coverage as shown for the CO on Ni(111).^{3,21} Hence, though there is no experimental proof, CO might adsorb on Ag(111) hollow sites as suggested in our structural model.

Finally, we want to discuss the question of whether the previously proposed CO adsorbate structures might also be suited to explaining the reported STM data. Schmeisser *et al.* suggested a herringbone structure for the CO monolayer on Ag(111) in analogy to the N_2 overlayer on graphite.^{8,22,23} This model was derived from angle-resolved photoemission spectra, exhibiting a similar structure as spectra of N_2 on graphite and notably a splitting of the CO 5σ orbital. In the herringbone structure, CO forms a $(\sqrt{3} \times \sqrt{3})R30^\circ$ (center of mass) overlayer. Due to an orientational in-plane ordering of the molecules, a $(2\sqrt{3} \times \sqrt{3})R30^\circ$ structure results, characterized by two glide planes. Consequently, different domains exist, which are rotated against each other by 60° and not by 18° as determined here. Thus this structure can be ruled out. Later experiments studying CO monolayers on Ag(111) did not give rise to distinct structural models. On the basis of ARUPS and HREELS, a disordered overlayer was suggested, where the CO molecules are adsorbed with a random orientation.⁹ LEED experiments indicated a well-ordered, incommensurate overlayer¹⁰ with intermolecular distances varying with the background pressure. The angle between the CO monolayer and the Ag(111) lattice was pinned at 9° , which agrees with the angle we determined from the STM images. However, since we clearly observe a commensurate growth in the STM, none of the results obtained from the previous experiments on CO/Ag(111) seems to explain our observations. Additionally, we consider the pinwheel structure, which is the CO phase on graphite found at a higher coverage. However, the model does not match the STM images, because either the angle to the Ag(111) substrate or the lattice constants of the overlayer cannot be reproduced. Thus, indeed, all the structural models proposed for CO on Ag(111) or graphite are not in accord with the superstructure determined with the STM.

In conclusion, we report the formation of well-ordered hexagonal CO islands on Ag(111) at temperatures above 17 K. The commensurate $(\sqrt{31} \times \sqrt{31})R9^\circ$ structure can be immediately derived from the STM images. A structural model is proposed, allowing for the imaging properties of

CO on silver, as well as the existence of two rotational domains. According to this model, CO hexamers represent the building blocks of the CO islands, whereby the two domains result from an alternate occupation of the fcc and hcp sites on the metal. The observation of small CO clusters—possibly CO hexamers or heptamers—gives further support for this assumption. Although the presented STM topographic images of CO on Ag(111) do not lead to an unam-

biguous structural model, they provide important information for theoretical studies investigating the CO adsorption on noble metals and the interaction between CO molecules.

We thank R. Liebenow who initiated the current work as well as H. Conrad and Th. Klüner for fruitful discussions. Financial support from the Studienstiftung des deutschen Volkes (M.K.) is gratefully acknowledged.

*Electronic address: kulawik@fhi-berlin.mpg.de

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¹²The total CO coverage cannot be determined, because a large fraction of the dosed CO is adsorbed on cold parts of the STM, and thus does not reach the sample surface.

¹³The onset temperature for the diffusion of CO molecules on Ag(111) was experimentally determined to be ~ 12 K. At 5 K,

however, CO can be displaced or even desorbed by interaction with the tip. Thus, the STM images in Fig. 1 do not depict the initial CO coverage of the surface, but one that is decreased due to the scan process.

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¹⁹Ordered CO islands can form at 5 K as a result of the interaction between tip and adsorbed CO. The chemical properties of the tip as well as the tunnel current seem to play a major role. Usually, these well-ordered islands were obtained after a large number of scans. After heating to 17 K, these islands were already observed in the very first scan on a new position on the surface.

²⁰The orientation with regard to the Ag(111) lattice was determined by comparison with atomically resolved STM images of the bare metal surface.

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