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Interaction of CO molecules with surface state electrons on Ag(111)

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Abstract

Like other close-packed noble metal surfaces, Ag(111) exhibits an occupied Shockley-type surface state that is believed to influence the adsorption of atoms and molecules. Using low-temperature scanning tunneling microscopy, we have directly probed this interaction by investigating the local CO distribution dependent on the Ag(111) surface state standing wave pattern forming in the neighborhood of strong scattering centers such as step edges or hexagonal holes. A quantitative analysis of the STM data reveals that the CO molecules are not arbitrarily distributed upon adsorption at 5 K; they adsorb preferentially near the minima of the standing wave pattern.
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Two-dimensional electronic states are formed on various metal surfaces due to the confinement of surface electrons between the vacuum on the one side and a partial bulk band gap on the other side [1]. Such a projected band gap is present, for instance, in noble metal (111) surfaces where the free-electron-like sp band does not cross the Fermi level, E_F, along the [111] direction. There is

unbroken interest in these so-called Shockley-type surface states because they strongly influence the electronic properties of the surface, which in turn affect adsorption and diffusion processes [2–4]. This was first deduced from field ion microscopy studies [5]. Scanning tunneling microscopy (STM) measurements were able to determine the influence of a the perturbed local density of states (LDOS) on chemisorption systems. Fascinating examples include the observation and theoretical description of long-range oscillatory interactions between single metal adatoms on noble metal

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(111) surfaces [6–10] or the formation of a Ce adatom superlattice on Ag(111) [11], both mediated by surface state electrons. In the case of physisorbed atoms or molecules, results from molecular beam experiments indicate that Shockley-type states contribute significantly to the charge density outside the surface, thus changing its physisorption potential [12,13]. However, spatial correlation between the physisorbed species and the surface state electrons could not be quantified thus far, though STM studies suggested such a spatial dependence [4]. A general description of the interaction between surface state electrons and adsorbates is of great interest since physisorption and chemisorption play central roles in heterogeneous catalysis.

The method of choice to investigate directly the influence of surface state electrons on the adsorption behavior of atoms and molecules is STM. The scanning tunneling microscope is sensitive to the LDOS at the surface. Accordingly, information on the surface state is accessible; due to the scattering of the nearly-free electron gas at defects or step edges, standing wave patterns are formed on the surface, which can be visualized by STM in real space [4,14,15]. Thus, the STM allows the determination of adsorption sites relative to the modulated LDOS.

In this letter, we present STM studies of the CO adsorption on Ag(111) at 5 K. The experiments focus on the direct interaction of CO with surface state electrons and therefore differ from previous studies that probe the indirect electronic interaction of chemisorbed adatoms via surface state electrons. Like other closed-packed noble metal surfaces, Ag(111) exhibits an occupied Shockley surface state, whereby the energy band sets in at −67 meV [16,17]. Adsorption of CO was investigated with respect to the interference pattern formed by the scattering of the electron gas at step edges and in hexagonal holes with monoatomic step height. Our results show that CO is not arbitrarily distributed about the surface but that the adsorption is indeed influenced by the two-dimensional surface state.

Experiments were performed with a custom-built Eigler-style STM [18], operated in ultra-high vacuum at 5 K. The Ag(111) sample was cleaned by cycles of alternating Ar ion sputtering and annealing to 780 K. In order to create additional scattering centers, the crystal was then sputtered with He ions at 400 K and cooled down to 5 K in order to freeze the resulting structure. This procedure led to the formation of hexagonal holes with monoatomic step heights. Finally, CO was dosed at 5 K such that a coverage of approximately 0.04 molecules/nm^2 was achieved. Due to the experimental setup, only a small fraction of CO molecules with an initial temperature of ∼300 K reach the Ag surface, while the majority are frozen on cold parts of the microscope. Careful annealing of the sample to 17 K mobilizes the CO molecules, enabling them to sample the potential due to the electronic perturbations; subsequently cooling the substrate for STM measurements freezes the molecules into a local equilibrium arrangement at the temperature at which motion is quenched. This temperature is estimated below.

Fig. 1a displays a typical STM image of the Ag(111) surface, which was prepared in this way. The standing wave pattern in the surface LDOS is clearly visible. The Fourier transform of this image is presented in Fig. 1b. It reveals the Fermi wavelength $\lambda_F/2 = 3.85$ nm of the Ag(111) surface state and was used to check the calibration of the microscope. The CO distribution in a hexagonal pit is shown in Fig. 1c. The CO molecules, imaged as depressions with a diameter of ∼0.7 nm, adsorb preferentially near the minima of the interference pattern.

Similar behavior is found close to step edges as shown in Fig. 1d. At bias voltages close to E_F, the CO molecules are located mainly in the troughs of the standing wave pattern. Accordingly, the surface state electrons at E_F seem to influence the adsorption of CO. On the other hand, it is not obvious whether surface state electrons with lower energy also participate in the CO–Ag(111) interaction. This question is addressed in the image series Fig. 2a–d. Here, the CO distribution is displayed for four different bias voltages in the range between the onset of the surface state and E_F. Though the amplitude of the modulated LDOS is reduced, the images agree well concerning the wavelength and the phase of the standing wave pattern, and CO is still found to adsorb preferen-
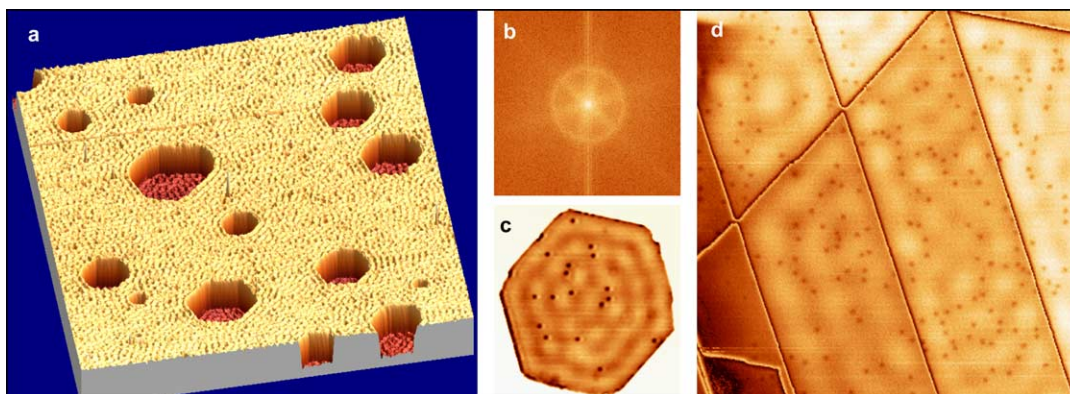
Fig. 1. (a) STM image ($V_S = 5$ mV, $I_T = 10$ pA, 240 nm × 240 nm) of a Ag(1 1 1) surface after He$^+$ sputtering at 400 K, cooling to 5 K and dosing with CO. The sputter procedure leads to the formation of hexagonal holes with monoatomic step height. The Shockley-type surface state of Ag(1 1 1) is visualized in the corresponding power spectrum (b) exhibiting a bright circle at $1/k = 3.85$ nm $= \lambda_F/2$. (c) Close-up of a hexagonal hole ($V_S = 10$ mV, $I_T = 10$ pA, 28.3 nm × 29.4 nm) revealing the CO distribution with respect to the standing wave pattern. (d) CO distribution on pristine terraces close to step edges ($V_S = 6$ mV, $I_T = 5$ pA, 50 nm × 50 nm). Step heights are reduced to increase the contrast on the terraces.

tially near the minima of this pattern. With regard to the interpretation of these results, it is important to note that the signal in the topography mode does not correspond to the LDOS at a certain sample bias V_S, but rather to the integrated density of states between E_F and the applied voltage. Hence, the topography image at -60 mV represents the LDOS integrated over almost the whole energy range of the occupied surface state, while the image at -10 mV corresponds to a good approximation to the LDOS at E_F [19]. The apparent similarity of the standing wave pattern in both images is in agreement with a simple theoretical model, predicting the same wavelength for the integrated LDOS and the LDOS at E_F.[1]

For the following quantitative analysis, V_S was chosen close to E_F since CO is easily dragged by the tip at more negative bias voltages (cf. Fig. 2d). Even if all electrons of the surface state interact with the CO, the preceding is justified be-

cause the CO distribution and the wave pattern observed at E_F is representative, as demonstrated above. Care also had to be taken when adjusting the tunneling current, I_T, since the CO molecules are easily dragged by the tip if I_T exceeds ~ 15 pA.

In order to investigate the CO adsorption dependence on the interference pattern quantitatively, the CO distribution has been analyzed in the neighborhood of strong scattering centers (i.e. step edges or hexagons) in the following way. We first filtered the images such that the CO molecules were removed, leaving only the standing wave pattern. Afterwards, line cuts were analyzed, running along the wave vector of the modulated LDOS at the former position of each CO molecule. The distance to the closest minimum was determined and normalized with respect to the Fermi wavelength $\lambda_F/2 = 3.85$ nm of the Ag(1 1 1) surface state. This normalization was necessary if the cut was not perfectly aligned with the wave vector, e.g. due to interference phenomena. Fig. 3 displays the results of this analysis. The histogram in Fig. 3a incorporates only CO molecules within the first three oscillations of the LDOS next to step edges, while Fig. 3b reflects the CO distribution in hexagonal pits with a surface area of at least 300 nm^2. The latter restriction was made in order to avoid the influence of electron

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[1] The correlation between modulations in the LDOS at E_F and the total charge density in the surface state band can be seen when integrating simplified wave functions in the band $\Psi_k \propto \sin kx$ over all possible wave vectors, i.e. between 0 and k_F at the Fermi level. Whereas the LDOS at the Fermi level corresponds to $|\sin(k_F x)|^2$, the total DOS has the form $L_0 + \frac{1}{4x}\sin 2k_F x$ and thus the same periodicity.
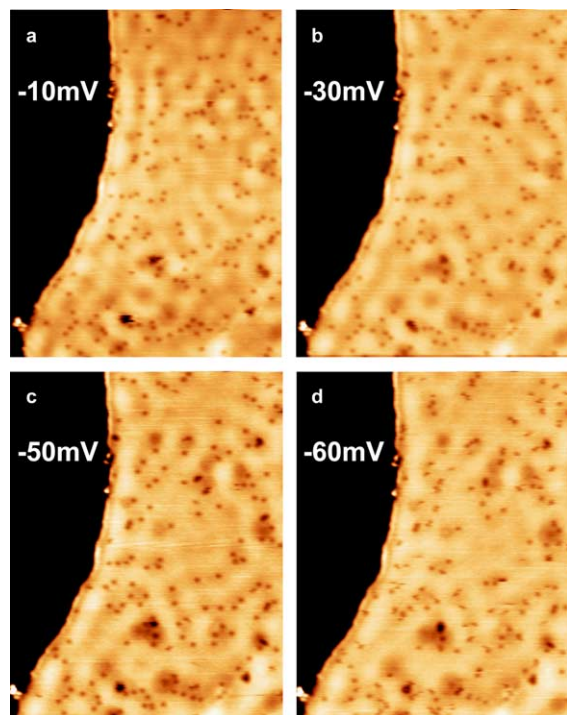
Fig. 2. STM images of a Ag(111) surface after being dosed with CO at ∼5 K, measured at the sample bias indicated ($I_T = 10$ pA, 36.6 nm × 49.7 nm). At all bias voltages the CO molecules (imaged as depressions) are mainly located in troughs of the surface state interference patterns. The latter changes only slightly when passing from −10 mV to −60 mV. Notably, the phase and the wavelength of the modulation remain the same. However, the amplitude of the standing waves is smaller at higher voltages and drops more rapidly with increasing distance from the step edge. Passing from (a) to (d) the position of some CO changes because they are dragged with the tip. This effect is still negligible at −10 mV, but becomes more important with increasing V_S. In part (d), the CO molecules appear smeared, indicating that the tip is dragging them during the scan.
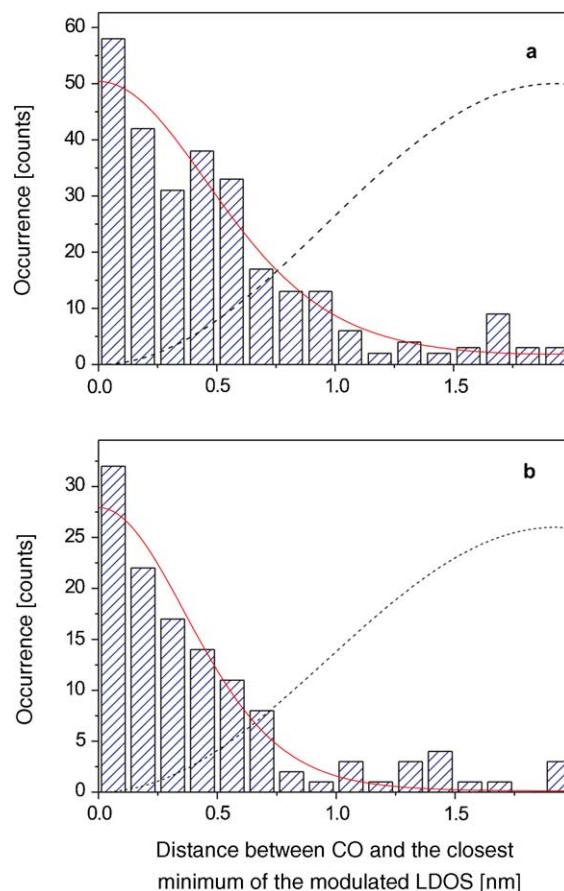

Fig. 3. Histograms of distances between CO adsorption sites and the closest minima of the standing wave pattern. Adsorption sites were analyzed near step edges ((a) 280 molecules) and in hexagonal pits ((b) 125 molecules). The solid lines depict a Boltzmann distribution fitted to the data. The dotted lines represent the wave pattern.

quantization effects present in small pits [15,20]. In both cases, the distributions reveal clear correlation between the modulated LDOS and the CO adsorption sites, whereby most of the CO molecules sit in the troughs of the interference pattern. It is important to note that only adsorption sites were taken into account where the modulation of the LDOS is dominated by a strong scatterer, i.e. a step edge and not by the CO itself. The latter also act as weak scatterers for surface state electrons. In this case, the LDOS is reduced at CO adsorption

sites, and the molecules sit near the minima of the standing wave patterns. Hence, counting these adsorption sites would naturally lead to a distribution that peaks in the troughs of the interference patterns. However, this is not of interest and, therefore, we considered only CO molecules with a maximum distance of 10 nm ($3\lambda_F/2$) to the nearest step edge.

The distribution of CO molecules with respect to the standing wave patterns enables an estimation of the energy difference ΔE between adsorption sites in minima and maxima of the surface state patterns. For this purpose, the experimental data are

fitted with a Boltzmann distribution $p(x) = e^{-E_{\text{pot}}(x)/k_B T}$ (Fig. 3). The spatial energy variation E_{pot} is assumed to show the same oscillatory behavior as the total DOS, hence $E_{\text{pot}} \propto \Delta E \sin(2k_F x)$, whereby a phase correction of $\pi/2$ has to be considered.[1] Additionally, E_{pot} decreases with the distance from the scattering center, e.g. the step edge. This distance dependence is neglected here, because only three oscillations of the LDOS modulation close to step edges were considered in the adsorption statistics. Applying this model, an energy difference of $\Delta E = 0.7 \pm 0.1$ meV is obtained in the vicinity of step edges, while $\Delta E = 1.2 \pm 0.2$ meV is calculated for the hexagonal pits. Surprisingly, the effect of the standing wave pattern is larger in hexagonal pits, although modulation of the LDOS typically appears larger on terraces above step edges [15]. We tentatively attribute this to amplifying interferences in the hexagonal pits due to the presence of different scatterers, which lead to stronger modulations of the LDOS. The contribution ΔE to the CO adsorption energy is at least one order of magnitude smaller than the diffusion barrier ($\sim$40 meV) of CO on Ag(1 1 1), as estimated from the onset temperature for CO diffusion of $\sim$12 K.[2] Thus, the surface-state-mediated modulations in the CO adsorption energy are not sufficient to induce long-range order of the molecules, but they influence the CO distribution on a length scale of λ_F. This explains why no higher CO concentration is observed close to step edges, where standing wave patterns are significant.

In the following section, we consider the interactions of CO with noble and transition metals in order to interpret the preferred adsorption of the CO molecules at sites with a lower LDOS. This interaction has been the subject of considerable controversy over the past decades. Commonly, a good description is provided by Blyholder [21], who attributes the CO-metal interaction to two attractive contributions: charge donation from the CO 5σ orbital to the metal and back-donation from the metal to the antibonding CO 2π* orbital. This model was extended later, pointing out that the σ-contribution is mostly repulsive in the case of late transition and noble metals [22–24]. Accordingly, the CO–Ag bond can be described in terms of a repulsive σ-interaction competing against an attractive π-interaction.

On Ag(1 1 1), CO is only weakly bound with a physisorption energy of −280 meV [25]. A large contribution to the CO–Ag interaction arises from sp-derived states that dominate the electronic structure close to E_F, whereas the 4d band sets in at about −4 eV below E_F. Due to the low energy of the Ag 4d electrons as well as their relatively small spatial extent, their interaction with the CO can be assumed to be small. Hence, major contributions arise from the 5sp band and from the sp-like surface state. With regard to the observed CO distribution, only the surface state electrons are of importance because only they contribute to the standing wave pattern. In principle, the interaction of the sp-like electrons with both the 5σ and the 2π* orbitals of the CO has to be considered. However, for an expected CO binding site on either on-top or hollow, the interaction between surface state orbitals and the 2π* orbital of CO is symmetry forbidden and therefore plays a negligible role. The main contribution is the σ-repulsion between the CO 5σ orbital and the filled surface state band, which favors CO adsorption in regions with a lower LDOS. Our experimental observations correspond to this interpretation, hence the σ-interaction appears to be decisive for the CO distribution with respect to the standing wave pattern. The repulsive interaction with the CO molecules is exerted by all electrons in the surface state band of Ag(1 1 1). The finding that the effect on adsorption energy and spatial distribution of CO is rather small is owed to the relatively small number of surface state electrons directly contributing to the charge density oscillations near step edges, which compete with a large constant interaction without spatial variation. It should be mentioned that due to the back-donation of electrons into the 2π* orbital of the CO, a repulsive electron–electron interaction might also occur between the CO 2π* orbital and

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[2] The onset temperature for the diffusion of CO molecules on Ag(1 1 1) was experimentally determined to be $\sim$12 K. The barrier to CO diffusion, E_{diff}, can be estimated by $E_{\text{diff}} = -k_B T \ln(\langle x \rangle^2 / 4 D_0 t)$. The pre-exponential factor D_0 was approximated by 10^{-3} cm^2 s^{-1} [26] and a mean jump length x corresponding to the Ag(1 1 1) lattice constant was chosen. This yields a diffusion barrier of $E_{\text{diff}} \sim 40$ meV.

the surface state band. This interaction is supposed to be of minor importance because of the extremely low occupation of the $2\pi^*$ orbital, but would also favor a CO adsorption in the troughs of the standing wave pattern.

The finding that filled surface states influence the repulsive part of physisorption potentials is consistent with earlier experiments of Bertel who compared the physisorption strength of Xe and the dissociation barrier of H_2 for various fcc(1 1 1) surfaces [1]. In both cases, Pd showed exceptional behavior: the adsorption enthalpy of Xe was significantly larger on Pd than on other metals, and H_2 dissociation on Pd proceeded via a non-activated precursor channel while an activated channel was found in the case of all other investigated surfaces. The anomalous behavior of Pd was assigned to the absence of an occupied sp surface state, leading to a reduced range of the repulsive forces in the physisorption potential as compared to transition metals with occupied surface states.

In conclusion, we report spatial correlation between CO adsorption at submonolayer coverages and standing wave patterns formed by the scattering of the quasi-two-dimensional electron gas of the Ag(1 1 1) surface state. STM measurements reveal that CO preferentially adsorbs at sites with a low LDOS, indicating that surface state electrons significantly influence the physisorption potential. It can be supposed that the interaction of the sp-like surface state with CO is of σ-character and therefore mostly repulsive. However, a corresponding theoretical study is necessary to evaluate all contributions.

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