Tailoring Confining Barriers for Surface States by Step Decoration: CO/Vicinal Cu(111)

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The influence of CO adsorption on the Shockley type surface state on vicinal Cu(111) surfaces is investigated using angle resolved photoemission. As the steps are decorated with CO the surface state shifts to higher binding energies, which is opposite to the known behavior on flat Cu(111). This is described within a one-dimensional potential model in which clean steps represent repulsive barriers and decorated steps become attractive wells. From the coverage dependence the integrated CO well potential can be quantified. It is $U_{CO}a = -2.9$ eV Å on both Cu(332) and Cu(221) surfaces. Density functional calculations reveal that this attractive potential is due to the very local charge transfer from the Cu step atom to the adsorbed molecule.

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The manipulation of electronic surface states using lateral nanostructures has attracted considerable interest since the first spectacular experiments of Eigler *et al.* [1]. Cu(111) surfaces provide a Shockley type surface state which behaves like a two-dimensional (2D) free-electron gas that is easily accessible to experiments [2,3]. The low density — one electron is shared by about 20 surface atoms — simplifies the interpretation of the experimental results. In most cases it is sufficient to consider the surface state as a sensitive spectator reacting to the scattering potentials of adsorbates or step edges. Mapping of the local density of states in single quantum objects using scanning tunneling spectroscopy (STS) allowed the characterization of energy-dependent scattering properties of isolated steps [4] and adatom rows [5]. In agreement with a theoretical study [6] it was found that single steps as well as many adsorbates are rather poor reflectors for electron waves with reflectivities at the Fermi level around $R \approx 0.4$.

Vicinal surfaces are miscut by a small angle relative to a high-symmetry crystal face. They are composed of low-index terraces of selectable width, bounded by equidistant steps with a preferential orientation, and present thus an easy access to a massive regular array of 1D nanostructures. The interaction of the surface state with the periodic step lattices of clean vicinal Cu(111) surfaces was investigated by photoemission [7–10]. Complementary to STS experiments on single nanostructures, which are mainly sensitive to the scattering phase shifts, the dispersive behavior of states propagating in a periodic step lattice gives a direct measure of the integrated potential barrier. Information about lateral potential variations could be obtained from the shape of the Fermi surface [10]. In this paper we demonstrate how these potentials are modified by the adsorption of CO molecules to the steps. They change from being repulsive in the clean case to being attractive upon CO adsorption.

The adsorption of CO on Cu(111) and its vicinal surfaces has been investigated in a number of studies [11–13]. The molecules are highly mobile at temperatures around 100 K and preferentially adsorb at step sites, bound with the carbon end to the outermost Cu atom of the upper terrace (step atom). Different ordered structures, where step sites are consecutively filled up to 75%, were identified on Cu(211), an *A*-type vicinal (111) surface [(100) step facets] with terraces that are three atoms wide [12]. Since the step atom has the same coordination number (7) on *A*- and *B*-type vicinal Cu(111) we expect similar ordered structures for *B*-type surfaces. On the flat surface, island formation with an $(\sqrt{3} \times \sqrt{3})R30°$ structure is observed down to 15 K [14]. Surface state energy shifts upon adsorption of CO on flat Cu(111) have been reported earlier by Paul *et al.* [15].

The three surfaces considered in this work are the flat Cu(111) surface and two *B*-type vicinals of Cu(111) that are composed of (111) terraces bound by monoatomic steps with (111) step facets. The nominal terrace widths are six and four atomic rows for Cu(332) and Cu(221), respectively, including the corner atoms below the step. The single crystal surfaces have been carefully prepared and characterized, as described in a previous publication [10]. The experiments have been performed in a modified VG ESCALAB 220 spectrometer [16]. All data were taken using He Iα radiation at a sample temperature of 110 K with the sample mounted on a liquid He cooled two-axis goniometer, with the exception of the clean-surface spectra that were measured at room temperature [Fig. 1(a), upper panel]. Spectra containing the surface state band bottoms were measured during continuous CO exposure with partial pressures increasing from 4×10^{-10} mbar at the initial stage of adsorption to 4×10^{-9} mbar at higher coverages. The energy/angle resolution was set to 60 meV/1° [full width at half maximum (FWHM)]. For each spectrum, the CO coverage was precisely determined by measuring the work function and using the previously determined work function versus coverage calibration curve.

Photoemission dispersion plots for the surface state on the three clean surfaces are shown in the top panels of Fig. 1(a). The wave vector component k_x is running

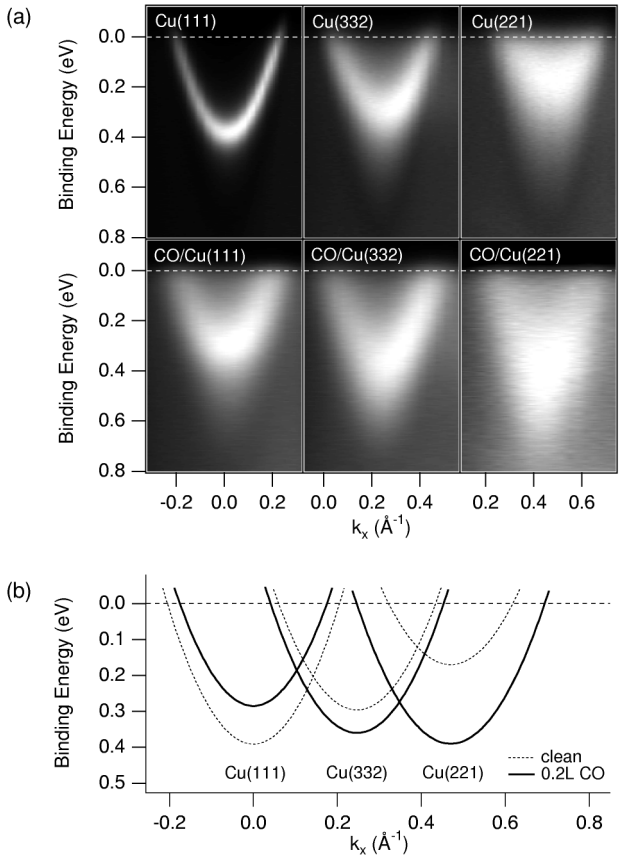

FIG. 1. (a) Measured photoemission dispersion plots (He Iα excitation), showing parabolic dispersion of the Shockley surface state on Cu(111) and two vicinal surfaces with and without CO adsorption (0.2 L). The wave vector component k_x is directed up the steps. Intensities are represented in a linear gray scale. (b) Compilation of the dispersion relations found on the clean (dotted lines) and CO-adsorbed (solid lines) surfaces, obtained from fitting the data shown in (a).

perpendicular to the steps, with the origin marking emission along the macroscopic surface normal. Parabolic dispersions in all three cases indicate propagation across step edges on the vicinal surfaces. On the two stepped surfaces the parabola are shifted on the momentum and on the energy scale. The momentum shifts point into the up-step direction and are a consequence of the tilt of the (111) terraces, though the exact values of the shifts are defined by the boundary of the Brillouin zone of the step lattice [7,8,10]. The energy shifts can be rationalized with Kronig-Penney-type models, as has been shown by Hörmandinger and Pendry [6]. The modification of the surface state band is well described with periodic rectangular potentials including a complex part to account for absorption. For describing the energy shift at the band bottom it is sufficient to use real potentials. To a first approximation the integrated step potential barrier $U_0 a$ is obtained from the energy shift ΔE_B of the surface state band bottom [17]: $\Delta E_B \approx U_0 a/\ell$ where ℓ denotes the 1D lattice constant [8]. Using the energy shifts of 71 and 198 meV for Cu(332) and Cu(221), respectively, we calculate repulsive step potential barriers of $U_0 a^{(332)} = 0.9$ eV Å and $U_0 a^{(221)} = 1.35$ eV Å in agreement with the literature.

In the lower panels of Fig. 1(a) the dispersion plots are shown for each of the three surfaces after the exposure to $\approx$0.2L (1L = 1 μtorr s) of CO. Figure 1(b) summarizes the changes of the dispersion relations upon CO exposure. The momentum shifts for the vicinal surfaces remain the same as in the clean cases, indicating that CO adsorption does not affect the step periodicities. The energy shifts show a different sign on the flat and on the vicinal surfaces. The downward shift signals that CO adsorbed at step sites makes them less repulsive, in fact even attractive (see below), whereas adsorption on terraces leads to an upward shift, in agreement with Ref. [15]. Figure 1(a) shows also that the photoemission linewidths increase strongly upon CO adsorption.

In order to study these effects more quantitatively, we have taken surface state spectra at the band bottoms for a continuously increasing CO exposure in the low-coverage regime where step sites are being filled. Figure 2 presents a selection of the spectra out of a more extensive set. The different sign of the energy shift can be seen in the raw data. For both vicinals, the minimum energy is below the band bottom of the clean (111) surface, from which we conclude that CO makes the step sites attractive. In the case of Cu(332) we see a deflection point at an exposure of $\approx$0.25 L, suggesting that terrace sites are being filled at higher coverages. Simultaneous with the change in energy we see on all three surfaces a strong decrease of the photoemission intensity and a broadening of the peak with increasing coverage. From the general trend we can argue that CO molecules act in all adsorption geometries as absorptive scatterers, coupling the surface state with bulk states [6].

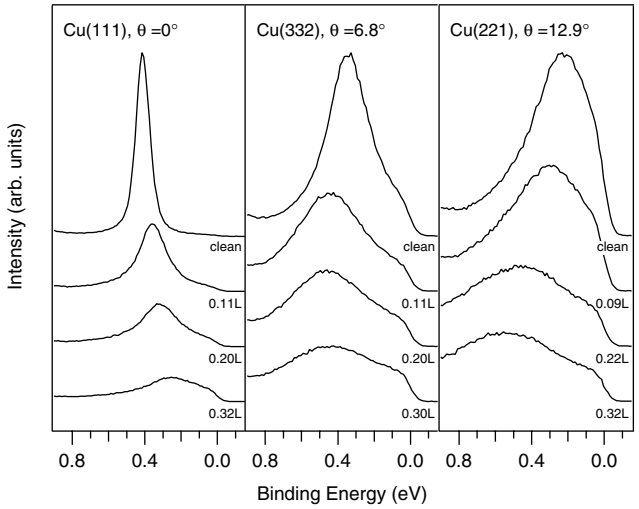

FIG. 2. Surface state spectra from Cu(111) and the two vicinal surfaces, measured at the band bottoms and as a function of CO exposure. The intensities are scaled to equal peak heights on the clean surfaces.

Binding energies and linewidths in the low coverage regime are shown in Fig. 3. To allow a comparison between flat and vicinal surfaces we define the coverage θ as the number of adsorbed molecules in the area of the (1×1) unit cell of Cu(111). Later on we will refer as well to the coverage θ^{sl} in the step-lattice unit cell. This is more illustrative to compare the vicinal surfaces, since θ^{sl} is proportional to the occupation of step sites. The two units are related by $\theta^{sl} = \theta \frac{2\ell}{\sqrt{3}a_S}$, where $a_S = 2.55$ Å is the surface lattice constant of Cu(111) and ℓ the step-step separation.

The data in Fig. 3(a) show for all three surfaces a linear dependence of surface state energy on θ [17]. The slope of -1.3 eV/ML is equal on both vicinal surfaces, whereas adsorption on Cu(111) leads to an increase in energy of 1.5 eV/ML. The linewidths in Fig. 3(b) correspond to the higher binding energy side HWHM of the Lorentzian surface state peaks, approximately 2/3 of which can be attributed to lifetime broadening [10]. For Cu(111) we find an increase in linewidth by almost an order of magnitude between the clean surface and a coverage of $\theta = 0.14$ ML

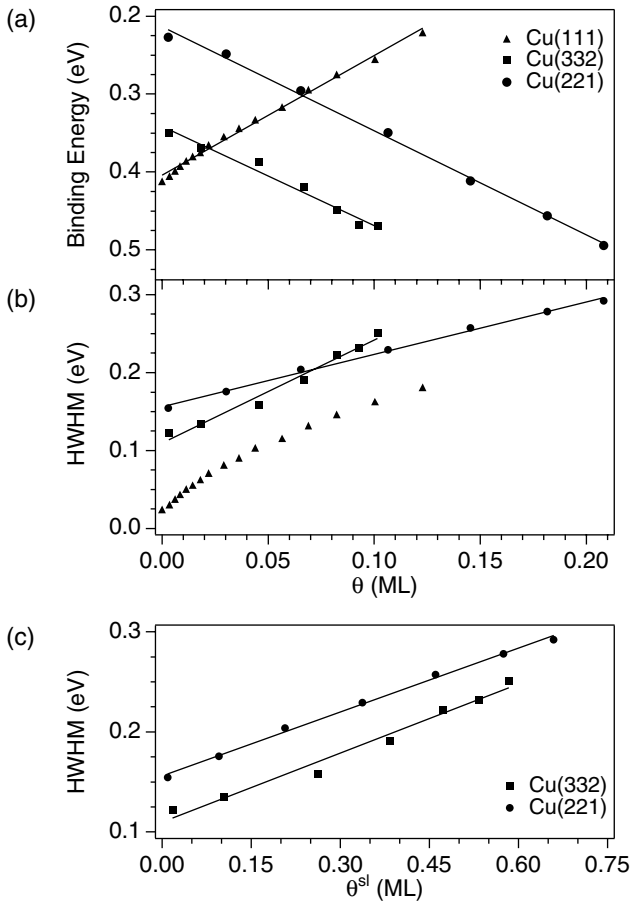

FIG. 3. (a),(b) Quantified surface state energy shifts and linewidths in the low-coverage regime. One monolayer corresponds to one CO in the area occupied by a surface atom on Cu(111). (c) Data from (b) shown as a function of the coverage θ^{sl} in the step-lattice unit cell.

where the surface state intensity decreases beyond recognition. On the vicinal surfaces the change in linewidth is less dramatic and can be well fitted by a straight line. In contrast to the binding energy we see a distinctly different increase of the linewidth on the two vicinal surfaces. However, the determined slopes of 1.3 eV/ML and 0.7 eV/ML for Cu(332) and Cu(221), respectively, scale exactly with the terrace lengths. The two curves show therefore the same slope when plotted versus θ^{sl} [Fig. 3(c)]. Summarizing we find that the change in binding energy is proportional to the CO coverage per unit area, whereas the linewidth change is proportional to the filling of step sites.

For describing the behavior of the surface state energy with CO coverage, we assign an independent potential barrier $U_{\mathrm{CO}}a$ to the step adsorbed molecules which we simply superimpose to the barrier of the bare step. The energy of the band bottom can now be written as

$$E_B \approx E^{(111)} + U_0 a/\ell + \theta^{sl} U_{\mathrm{CO}} a/\ell\,. \qquad (1)$$

With $\theta^{sl} \propto \ell\theta$ it follows that $\Delta E_B \propto \theta$ as it is observed in the experiment. From the determined change in surface state energy of -1.3 eV/ML we calculate an attractive scattering potential of $U_{\mathrm{CO}}a = -2.9$ eV Å for step adsorbed CO.

Why does the step potential become attractive upon CO decoration? To address this question, a Cu(332) slab with CO adsorbed on top of a step atom on both sides of the slab was studied by DMol3 density functional theory (DFT) calculations [18], and compared to one for the same bare substrate. The unit cell for the seven-layer slab consists of 78 Cu atoms and two CO molecules in the first case. A significant charge transfer from the step atom to the CO molecule is observed. As a consequence an attractive potential builds up at this site. The very local change of the electrostatic potential, as obtained from the DFT calculations, is shown in Fig. 4. Note that the much stronger potential change within the molecule is simply due to the addition of the ionic C and O core potentials. In the calculations, the net potential change can be conveniently probed by the core level shifts of the Cu step atoms. Both, the calculated $3s$ and $3p$ levels shift by 0.6 eV to higher binding as compared to the respective median energies. The center of gravity of the step atom d-partial density of states shifts by about 1 eV to higher binding energy on CO adsorption. Unfortunately, the surface state remains hard to identify in these calculations because of excessive symmetry folding in this vicinal geometry. Nevertheless, these results give evidence that the rather localized charge transfer at the step atom is responsible for the additional attractive potential at the adsorption site when CO is present.

The opposite sign of the energy shift on flat Cu(111) can be explained with the different adsorption geometry. In agreement with earlier photoemission data [15] we find complete quenching of the surface state wave function in the $\sqrt{3} \times \sqrt{3}$ phase (Fig. 2). STS measurements in the vicinity of a single CO molecule on Cu(111) showed a

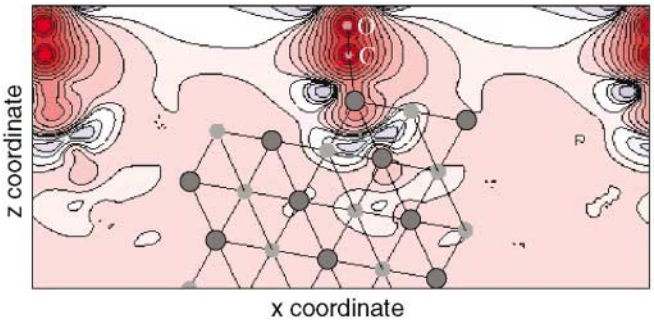

FIG. 4 (color). Change in the electrostatic potential on a vicinal surface due to the presence of CO adsorbed at the steps. DFT calculations have been performed for the bare vicinal surface and for an unrelaxed vicinal surface with optimized bonding geometry for the CO molecule. The potential difference is plotted within a $(1\bar{1}0)$ plane perpendicular to both, the Cu(332) surface and the steps. A logarithmic contour spacing is used, whith red shading representing attractive values for electrons, blue shading repulsive ones. The contour around the Cu step atom lies at 2.7 eV. The Cu lattice is indicated, the dark atoms lie in the same plane as the CO molecule.

strong reduction of the surface state spectral weight, but no significant change in binding energy on approaching the adsorbed molecule [19]. Thus only a small part of the surface state wave function samples the attractive real part of the scattering potential. Consequently, the expectation value of the energy can be approximated by the change in kinetic energy on bare surface areas, as it was found for homoepitaxy on Cu(111) [20]. This change is always positive and greater than zero as soon as the wave function scatters off coherently from more than one phase boundary. For circular bare surface areas of radius r the energy shift is proportional to $1/r^2$ [20]. Assuming random growth one expects $r \propto 1/\sqrt{\theta}$ and thus $\Delta E_B^{(111)} \propto \theta$ as we find experimentally.

The surface state linewidths will be discussed following the ideas of Hörmandinger and Pendry [6]. Recently we found a strong reduction of the photohole lifetime on clean vicinal Cu(111) as compared to the flat surface and attributed this effect mainly to scattering into bulk states [10]. The influence of step decoration on the lifetimes is twofold. Step adsorbed molecules can enhance the coupling of the surface state wave function with bulk states and they modify the Bloch wave functions. Because of the repulsive step potentials on the clean vicinal surfaces, the surface state charge density is mainly concentrated on the terraces and decreases towards the steps, whereas for attractive potentials, i.e., upon CO adsorption, the situation is reversed. The change of the local density at step sites is proportional to the reduction of the confining barrier ($\theta^{sl} U_{\mathrm{CO}} a$). Thus the change of the decay rate of the surface state photohole should depend directly on the CO occupancy of step sites (θ^{sl}), independent of the terrace length, as we find experimentally (Fig. 3). In contrast the linewidth observed for CO/Cu(111) has to be attributed mainly to inhomogeneous broadening. Bare islands of different size and shape lead to different confinement shifts and since photoemission is a spatially averaging technique we find a broad linewidth reflecting the island size distribution [20].

In conclusion, we have given further evidence that the step lattices on vicinal surfaces can be well described by 1D periodic potentials felt by the surface state electrons. It is demonstrated that low temperature exposure to CO leads to step decoration where adsorption to the step atoms contributes a strongly attractive potential well of $U_{\mathrm{CO}} a = -2.9$ eV Å to the previously repulsive barriers. The combined potential is attractive for both investigated surfaces, which is further confirmed by the coverage dependence of the linewidths and by DFT calculations. It will be interesting to compare these results with STS experiments in step-decorated single nanostructures.

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