Enhanced Optical Sensitivity to Adsorption due to Depolarization of Anisotropic Surface States

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Reflectance difference spectroscopy is used to probe the optical transitions between surface states on the Cu(110) surface. Upon deposition of smallest amounts of carbon monoxide (CO) the signal is strongly quenched, which translates into a huge cross section of the order of 1000 Å^2 for a single adsorbed CO molecule. This strongly enhanced surface sensitivity is interpreted as the loss in anisotropy (depolarization) of the surface states due to scattering from the adsorbed CO molecules. This feature renders RDS an extremely sensitive tool to probe the adsorption kinetics on anisotropic metal surfaces.

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The electronic structure at surfaces may strongly differ from that of the corresponding bulk material. In particular, so-called *surface states* may emerge as a consequence of the symmetry breaking at the surface. Whereas on covalently bonded crystals surface states are rather localized, these states may extend over large lateral distances on metal surfaces and behave like a two-dimensional quasifree electron gas confined to the topmost few surface layers. Scanning tunneling microscopy (STM) and spectroscopy (STS) have provided fascinating images visualizing the standing waves of surface state electrons confined in quantum corrals as well as the interference fringes of surface electron waves scattered from step edges or point defects [1].

Optical probes are also well suited to investigate the electronic structure of solids. Unfortunately, the large photon penetration depth often reduces the surface sensitivity of the simple linear optical techniques and more complicated nonlinear techniques have to be employed. This is not the case in reflectance difference spectroscopy (RDS), which measures the *difference* in the normal-incidence reflectivity for two mutually perpendicular orientations of the polarization vector as a function of photon energy [2,3]. For cubic crystals the optical response from the bulk cancels by symmetry and the signal thus arises from the lower symmetry of the surface. This makes RDS a surface sensitive optical probe of the surface structure, morphology, and electronic properties. The technique is widely used in the study of semiconductor surfaces and their growth in various environments. More recently, RDS has also been applied to metal surfaces such as Cu(110) [4,5], Ag(110) [6–8], and Au(110) [9,10]. It has been demonstrated that RDS is sensitive to structural changes during sputtering, surface reconstruction, and the adsorption of atoms and molecules such as oxygen, CO, and organic molecules [11].

On the fcc(110) surfaces, the difference of the (complex) reflectivities is measured for light polarized along the two orthogonal surface orientations $[1\bar{1}0]$ and $[001]$, respectively:

$$\frac{\Delta r}{r} = \frac{r_{[1\bar{1}0]} - r_{[001]}}{2(r_{[1\bar{1}0]} + r_{[001]})}. \tag{1}$$

The real part of the RDS spectrum obtained from the clean Cu(110) surface is shown in Fig. 1 (open circles). It has been interpreted in terms of direct electronic transitions involving surface states as well as bulk related states which are modified in the surface region. The most pronounced feature occurs at a photon energy around 2.1 eV. It is contributed by a transition between an occupied and

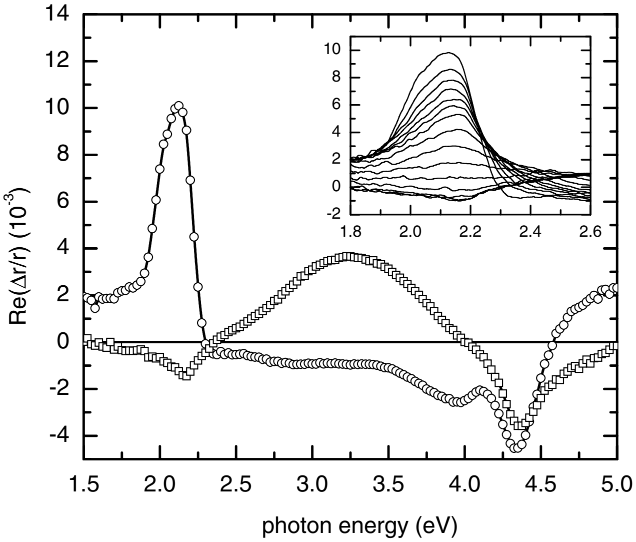

FIG. 1. Real part of the RDS spectra recorded at 12 K from the clean Cu(110) surface (circles) and after adsorption of 2 L of CO at 12 K (squares). The inset shows the evolution of the RDS feature around 2.1 eV after CO exposures of 0, 0.007, 0.012, 0.018, 0.028, 0.038, 0.059, 0.111, 0.205, 0.375, 0.505, 0.805, 1.305, 1.805, and 2.305 L of CO (from top to bottom).

an unoccupied surface state located at the $\overline{Y}$ symmetry point of the surface Brillouin zone and by a modified bulk transition related to the onset of the interband transitions ($\Delta_5 - \Delta_1$) in copper in the vicinity of the bulk symmetry point X. The unoccupied surface state at $\overline{Y}$ has p_y symmetry and the surface state transition at 2.1 eV can be excited only by light polarized along the y direction, i.e., for light polarized along the [001] direction of the surface plane. Because of this intrinsic anisotropy, the surface state transition gives rise to a strong contribution to the RDS signal.

In a previous investigation [4], the adsorption of oxygen on Cu(110) surface was found to lead to a complete quenching of the RDS signal at 2.1 eV and it was concluded that "the real-time investigation of the dynamics of surface processes is the most promising future application of RDS on metal surfaces." It might be assumed that the quenching of the RDS signal is proportional to the actual adsorbate coverage. This is, indeed, true for a transition involving a localized surface state (such as on a semiconductor surface) or a bulk d-band transition (as for the RDS negative peak at 4.3 eV in Fig. 1). However, we will demonstrate that the sensitivity of the RDS signal at 2.1 eV to adsorbates or surface defects can be extremely large: in the case of CO adsorption on Cu(110), the RDS signal at 2.1 eV decreases with an initial slope which is more than 50 times larger than if it were directly proportional to the CO coverage. This surprising result will be explained in terms of the delocalized (free electron-like) nature of the surface state electrons on metal surfaces. As a consequence, RDS provides a hitherto unrecognized sensitivity to study the kinetics of adsorption, structure formation, and desorption on metal surfaces.

The experiments were performed in a UHV apparatus with a base pressure below 1×10^{-10} mbar. The high quality Cu(110) sample (miscut angle $<0.1°$) was cleaned *in situ* by repeated cycles of Ar ion bombardment and subsequent annealing at 900 K. The cleanliness and surface crystalline quality was checked by AES and LEED. The sample temperature can be varied between 12 and 1000 K using a combination of liquid He cooling and electron beam heating. CO was adsorbed by exposing the surface to a constant CO pressure of the order of 1×10^{-9} mbar. The RDS spectrometer was mounted outside the UHV system in front of a low-strain quartz window.

Figure 1 shows the real part of the RDS signal $\Delta r/r$ for the clean Cu(110)-(1×1) surface and after adsorption of 2 L of CO at 12 K ($1\ \mathrm{L} = 10^{-6}$ torr $\cdot$ s). As can be seen in the inset, adsorption of submonolayer amounts of CO leads to significant changes in the RDS spectrum, especially in the vicinity (± 0.1 eV) of the 2.1 eV peak.

The RDS signal can also be monitored at fixed photon energy in order to follow the adsorption process in real time. The RDS intensity at a photon energy of 2.13 eV is shown in Fig. 2(a). Since the sticking coefficient for CO on Cu(110) at these temperatures is constant and close to unity [12] there is a simple, linear relationship between exposure and coverage (bottom vs top axis in Fig. 2). For calibration of the coverage scale, the formation of the well known (2×1) phase (obtained after annealing the CO adlayer to temperatures above 110 K) was monitored with LEED and He diffraction. Its saturation ($\Theta = 0.5$) was found to occur at an exposure of 1.7 L and is defined as 1 ML in Fig. 2. It coincides with the intermediate maximum of the He reflectivity in Fig. 2(b). If the change of the RDS signal were proportional to surface coverage one would expect a *linear* decrease of the RDS intensity with the CO exposure. Yet, it is quite clear from Fig. 2(a) that the RDS signal at 2.13 eV during CO exposure at 12 K, does not follow a simple linear behavior. Most surprising is the steep initial decay up to a coverage of about 0.003 ML (exposures ≤ 0.005 L), with a slope which is about 50 times larger than expected for a linear decay up to the (2×1) monolayer saturation reached at 1.7 L [see inset in Fig. 2(a)]. At a coverage of about 0.003 ML, the curve exhibits a kink after which the signal decays with a reduced slope, but still much faster than linear.

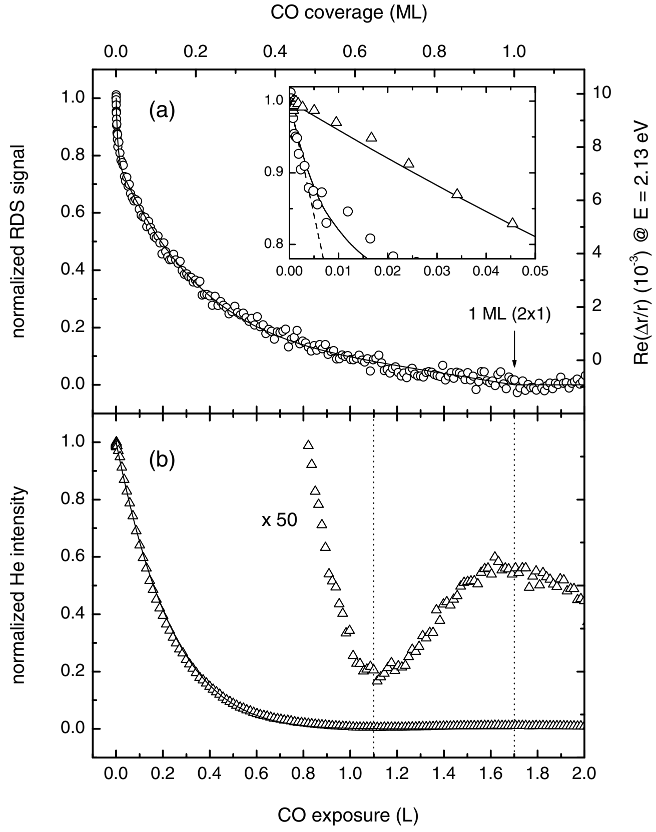

FIG. 2. (a) RDS signal recorded during adsorption of CO at 12 K at a photon energy of 2.13 eV. (b) Normalized specular He intensity monitored during adsorption of CO at 50 K. The inset in (a) shows a zoom-in of the initial decay of the RDS signal (circles) and the He intensity (triangles). Lines are fits to the data based on the cross section overlap model [Eq. (2)] as described in the text.

The over-proportional decay of the RDS signal is reminiscent of the variation of the intensity of a thermal He atom beam specularly reflected from a flat metal surface during adsorption [13,14]. For comparison, we show in Fig. 2(b) the variation of the normalized He reflectivity during CO exposure on the Cu(110) surface at 40 K [15], noting that similar curves have also been obtained by Kunat *et al.* [12]. For thermal He atoms the enhanced sensitivity is understood as being due to the diffuse scattering from isolated surface defects or adsorbates. The effective surface area or *cross section* Σ from which the He atoms are scattered off the specular direction is typically a factor of 10 larger than the actual surface area σ occupied by the defect or adsorbate. In the case of a random distribution of adsorbates on the surface, the normalized reflected He intensity can be described by [14]

$$I/I_0 = (1 - \Theta)^{n_s\Sigma} \approx 1 - n_s\Sigma\Theta, \tag{2}$$

where n_s denotes the surface density of the adsorbates and Θ is the coverage in monolayer units. The second part of Eq. (2) holds for low coverages, i.e., $\Theta \ll 1$. The solid line through the data points in Fig. 2(b) shows a fit to Eq. (2) with $n_s = 5.4 \times 10^{14}$ cm^{-2} [the CO density in the (2×1) phase] yielding a cross section $\Sigma = 130$ Å^2 which is about 7 times the size of the (2×1) unit cell. Note that Eq. (2) describes the decrease of the reflectivity assuming *random* adsorption into a lattice gas. The continuous decrease of the slope for higher coverages is the result of the increasing statistical overlap of the cross sections Σ of the individual CO molecules.

The normalized RDS intensity at 2.13 eV can be described in a similar way as the He reflectivity by defining an effective cross section, i.e., an area on the surface which describes the effect of the adsorption of an isolated CO molecule. For a quantitative fit of the signal [solid line in Fig. 2(a) and the inset], two cross sections $\Sigma_0 = 4620$ Å^2 and $\Sigma_1 = 97$ Å^2, respectively, have to be introduced. In addition, a linear decay describing the contribution of the bulk related optical transition to the RDS signal at 2.13 eV has to be included. The weighted sum $s_0(1 - \Theta)^{n_s\Sigma_0} + s_1(1 - \Theta)^{n_s\Sigma_1} + (1 - s_0 - s_1)(1 - \Theta)$ with $s_0 = 0.213$ and $s_1 = 0.562$ then provides a good overall fit of the change of the RDS signal and accounts for the kink observed at a CO coverage of about 0.003 ML. For comparison, the dashed line in the inset of Fig. 2(a) shows the initial decay for an *average* cross section of 1000 Å^2 which is about 50 times larger than the actual size $\sigma = 18.5$ Å^2 of a CO molecule in the (2×1) phase.

Having shown the large sensitivity of the RDS signal at 2.13 eV to the adsorption of CO, we now have to identify the origin of the two cross sections Σ_0 and Σ_1 and rationalize their numerical values. The cross section Σ_1 corresponds to a circle around the adsorbed CO molecule with a radius of a few Cu lattice spacings. This can be interpreted as the lateral size of the electronic perturbation (scattering potential) introduced by an isolated CO molecule. Indeed, scanning tunneling spectroscopy has shown that this is the characteristic size across which the surface local density of states (LDOS) is completely quenched by the presence of a surface defect or adsorbate [16]. We then expect the optical transitions to be quenched over the same area, leading to a reduction of the RDS signal according to Eq. (2) with $\Sigma = \Sigma_1$.

The more intriguing question is how to explain the huge cross section Σ_0 which is again 50 times larger than Σ_1 and, hence, corresponds to a size of the order of several 100 substrate unit cells. It is unreasonable to believe that the LDOS could be quenched over such a large area by a single adsorbed molecule. On the other hand, we have to bear in mind, that RDS does not measure the *intensity* of an optical transition but rather its *anisotropy*. Hence, it is not the combined density of states which matters but the fact to what extend the associated transition can be excited with light polarized along x and y, respectively. In the case of Cu(110) a certain fraction of the RDS signal at 2.13 eV arises from a transition involving surface states at the $\overline{Y}$ point. As mentioned earlier, on the perfect Cu(110) surface (extended terraces) the associated optical transition is highly anisotropic and can be excited only with light polarized along the [001] (y) direction. This situation changes dramatically in the presence of a point defect or an isolated CO molecule. The local symmetry is broken and the surface electron waves will be scattered into a more isotropic distribution. As a result, the initial anisotropy is lost and the RDS signal is considerably affected. This is illustrated by the simple model depicted in Fig. 3(a). Here we consider an incident surface state electron described by a free electron wave $\psi(\mathbf{r}) = \exp(i\mathbf{k}_i\mathbf{r})$ with wave vector $\mathbf{k}_i = k_Y\mathbf{e}_y$ corresponding to the $\overline{Y}$ point of the surface Brillouin zone at $k_Y = 0.87$ Å^{-1}. Assuming a circular hard-wall potential with radius R, the amplitude of the scattered wave as a function of the scattering angle θ can be written as

$$I(\theta) = \left| \sqrt{\frac{kR}{\pi}} \int_{(\pi/2)-\theta}^{\pi/2} \cos(\alpha)\, e^{ikR[\cos(\alpha)-\cos(\alpha+\theta)]} d\alpha \right|^2, \tag{3}$$

with $k = |\mathbf{k}_i| = |\mathbf{k}_f|$ and the other symbols as defined in Fig. 3(b). The result is shown in Fig. 3(c) together with the classical result $I(\theta) \propto \sin(\theta/2)$ in which the electrons are treated as particles specularly reflected from a circular boundary. The polarization anisotropy of a partial wave scattered into an angle θ is given by $p(\theta) = 1 - 2\sin^2(\theta)$ and the average polarization of the scattered wave is obtained by weighting $p(\theta)$ with the intensity distribution $I(\theta)$ and integration over all scattering angles θ. The result is very close to zero, i.e., after scattering from the circular hard wall, the highly polarized incident wave becomes completely depolarized and the *anisotropy* of

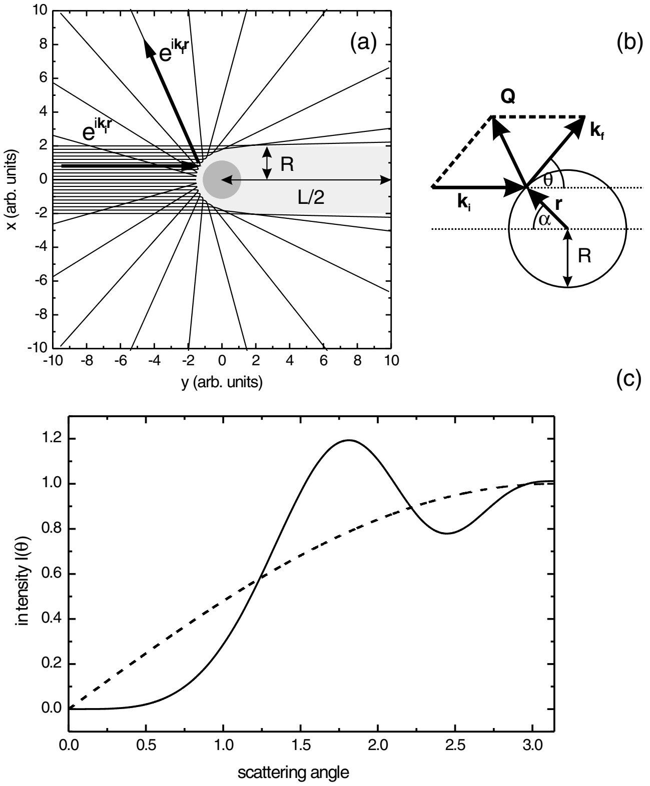

FIG. 3. (a) Model illustrating the scattering of a surface electron wave from a single CO molecule located at $(x, y) = (0, 0)$. (b) Definition of the scattering parameters. (c) Angular distribution of the scattered intensity obtained by numerical integration of Eq. (3) using $R = 5$ Å (solid line) and classical result (dashed line).

the RDS signal is efficiently quenched. The corresponding cross section Σ_0 can be estimated as follows [see Fig. 3(a)]: The anisotropy of the incident electron wave is perturbed over an area which corresponds to the shadow cast by the scatterer [gray region in Fig. 3(a)], i.e., $\Sigma_0 \approx 2R \times L/2 = R \times L$, where L is a measure of the average terrace width or the typical distance between residual defects on the surface. Taking realistic values for the radius of the scattering potential $R \sim 5$ Å and $L \sim 200$–500 Å, values for Σ_0 of the order of 1000 Å^2 and above are obtained, in agreement with the values determined from the present experiments.

In summary, we have shown that reflectance difference spectroscopy can be extremely sensitive to the presence of minute amounts of surface defects or impurities. In fact, we have obtained similar results for metallic and inorganic adsorbates other than CO as well as after sputtering the Cu(110) surface at low temperature. The strongly enhanced sensitivity to surface defects appears to be related to the delocalized nature of the surface electrons, in particular, of surface states with a large intrinsic anisotropy. This offers the potential to study the characteristics of surface electronic states on a macroscopic scale and, most importantly, it provides new opportunities to use RDS as an extremely sensitive surface analytical tool for adsorption studies on anisotropic metal surfaces. Indeed, the large cross sections observed here allow minute coverages of the order of 10^{-4} of a monolayer to be easily detected *in situ* and in real time. In addition, changes in the lateral distribution due to island condensation or the onset of adatom mobility (which do not change the coverage but only the cross-section overlap) can be monitored in a similar way as with thermal He atom scattering [14]. For instance, we were able to detect the onset of the mobility of CO on Cu(110) (and the resulting aggregation of the molecules into chains running along the [001] direction) by a noticeable increase of the RDS signal at 2.13 eV at around 60 K.

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