Optical Response of the Copper Surface to Carbon Monoxide Deposition

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The optical response of the Cu surface upon CO deposition is investigated from the clean Cu(110) to the reconstructed CO/Cu(110)-$p(2 \times 1)$ geometry through *ab initio* electronic structure calculations. We ascribe the relevant structures in the calculated reflectance anisotropy spectrum of the reconstructed phase to the persistence of surface states transitions. These are excited by light polarized along the direction perpendicular to the one found at the clean surface. We devise a simple model for the evolution of the optical response in the adsorption process, identifying three different regimes. The *impurity regime*, at very low coverages, is characterized by a critical coverage that enhances the actual one by a factor of $\simeq 30$, close to the value estimated experimentally.

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Adsorbates are known to induce passivation of surfaces, i.e., the suppression of the electronic surface states, as opposite to bulk states, forming at the clean surface by the breaking of translational symmetry along the normal to the surface. Formation and quenching, by coverage, of such states can be probed by the reflectance anisotropy spectroscopy (RAS), a difference technique [1] that avoids the effect of penetration into the bulk and is very sensitive to changes in the surface morphology. In the framework of clean surfaces, a RA spectrum has been considered as the signature of the surface, and coverage, typically by oxygen, as an experimental direct tool to discriminate between surface- and bulk-derived RA features of the substrate, as in the well-known case of O/Cu(110) [2]. To-date technological applications of molecular electronics [3,4] involve deposition of ringlike or chainlike molecules of variable size on metallic (or semiconducting) substrates. The need for interface analysis at submonolayer level is impressing a new impulse to RAS to focus on subtle issues of the chemisorption process. Much experimental work is being concentrated on the kinetics of absorption and reorientation of the molecules upon coverage on the Cu(110) [5–7] surface. Noble metals are ideal substrates for molecular systems in nanotechnologies and many fundamental aspects of the chemisorption process on Cu may apply as well to Ag and Au [8,9]. An interesting, still open question is the nonlinearity of the RA response vs coverage, for different adsorbates on Cu(110), as observed by Frederick *et al.* [5] and Sun *et al.* [7], at variance with results by Jin *et al.* [10] and with the expected, linear behavior in semiconductors. Despite the flourishing experimental situation, the theoretical interpretation of the RA spectra is not straightforward. The successful, first *ab initio* calculation of RA spectra in Cu and Ag(110) surfaces [11] showed that theory is finally capable to calculate reliable RA spectra of metallic systems without adjustable parameters.

In this Letter we address the carbon monoxide chemisorption on the copper surface and, based for the first time on *ab initio* calculations, we propose a theoretical model for the evolution of the RA spectrum from the clean to the one monolayer covered surface. As observed by Sun *et al.* [7] and in good agreement with those results, the 2 eV peak, ascribed to surface state transitions in clean Cu(110), is found to decrease strongly nonlinearly at low coverages. The same feature is also observed in other systems [5,6,12,13] adsorbed on Cu(110). We also show that CO adsorption affects profoundly the dynamics of the optical transitions with respect to the clean surface in the whole RA spectrum (0–6 eV). We recognize the signature of the CO molecule on Cu by ascribing the RA peaks to the formation of electronic surface states peculiar of the modified interface as also observed in larger molecular systems with carboxylic groups. Most interestingly, we interpret the observed chemisorption kinetics [7] by describing quantitatively the RA spectra at three different regimes of CO coverage. We therefore propose CO/Cu as a prototype for further investigations on the adsorption kinetics on metallic surfaces monitored by RAS.

The CO/Cu(110) surface with reconstruction [14] $p(2 \times 1)$ is shown in the inset of Fig. 1. In this geometry CO occupies on-top positions at Cu sites forming alternating chains along the [001] surface direction. Electronic and optical properties have been calculated through the *ab initio* full potential linear muffin tin orbital [15] method within the density functional theory [16] in the local density approximation for the exchange-correlation potential [17], with the same accuracy used in previous calculations [11,18] for metallic systems. The interface is modeled by the *slab technique* including nine Cu layers (bulk Cu lattice constant $a = 3.62$ Å) sandwiched symmetrically by a sequence of one layer each of C and O, respectively, followed by a vacuum region of thickness 7.68 Å, equivalent to six atomic layers. The only reported [14] value of a downward relaxation of only the first [19] Cu layer, $\simeq 10\%$ of the bulk interlayer distance, is comparable to that of the same layer in clean Cu(110) surface

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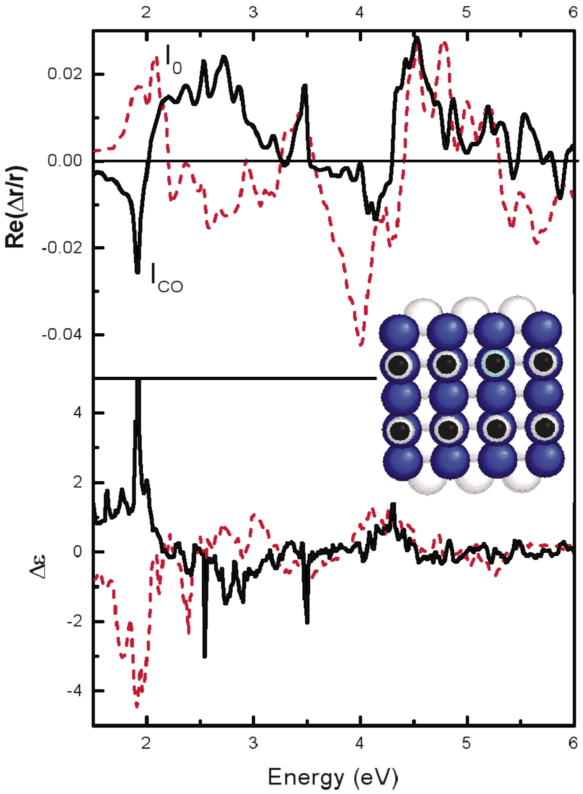

FIG. 1 (color online). Calculated reflectance anisotropy spectra (top) and surface dielectric anisotropy curves (bottom) of clean Cu(110) (dashed) and CO/Cu(110)-$p(2 \times 1)$ (solid) surfaces. Inset: Cu sublayer (white spheres), Cu surface layer (dark spheres), and on-top CO molecules (centered spheres) in the CO/Cu(110) surface.

[20]. There, relaxation was found irrelevant to the RAS. We disregard relaxation in the present calculations. RAS measures the difference Δr of the reflectivities $r_{[1\bar{1}0]}$ and $r_{[001]}$ along two inequivalent directions of the unsymmetrical fcc (110) surface. The spectrum is given by [1]

$$\mathrm{Re}\left(\frac{\Delta r}{r}\right) = \frac{r_{[1\bar{1}0]} - r_{[001]}}{2(r_{[1\bar{1}0]} + r_{[001]})} = \frac{4\pi\omega d}{c}\mathrm{Im}\left(\frac{\Delta\epsilon}{\epsilon^b - 1}\right),$$

where $\Delta\epsilon = \epsilon_{[1\bar{1}0]} - \epsilon_{[001]}$, the surface dielectric anisotropy (SDA), and ϵ^b, the bulk dielectric function, are calculated *ab initio* and d and c are constants. d, of the order of a few Å, is introduced [11,21] to yield a dimensionless SDA. In semiconductors, where the dielectric tensor $\epsilon(\omega)$ is determined only by interband transitions, the sign of $\Delta r/r$ (RA) coincides with that of $\Delta\epsilon$ indicating directly along which of either surface direction the light absorption is more intense. In metals the RA, including its sign, is determined by the interplay between interband and intraband transitions. The former ones are overwhelming in $\Delta\epsilon$ whereas the latter ones dominate in ϵ^b at low energy where optical transitions occur among surface states. The relationship between RA and SDA in the clean (110) surface of Ag and Cu has been explained theoretically in recent calculations [11].

In the top (bottom) panel of Fig. 1 we show the RA's (SDA's) of CO/Cu(110)-$p(2 \times 1)$ and clean Cu(110) [11] surfaces. Three relevant features of the RA spectrum of CO/Cu(110), in very good agreement with the measurements [7], are to be focused on and compared with the clean surface: (a) the initial negative slope of the curve with a minimum at 1.9 eV (henceforth referred to as I_{CO}), followed by (b) a wide positive shoulder extending up to $\simeq 3.5$ eV, then decreasing into (c) a shallow negative structure around 4 eV, reminiscent of the minimum in the clean surface. In clean Cu(110) the positive RA peak (henceforth denoted by I_0) at $\simeq 2$ eV, ascribed to transitions among surface states [11,22] located at $\bar{Y}$, is compatible [7], by symmetry, with maximum light absorption for polarization along the [001] direction in agreement with $\Delta\epsilon < 0$ (see Fig. 1, bottom). In the CO/Cu case, instead, the signs of RA and SDA from 1.5 to $\simeq 3.5$ eV are opposite to those in the clean surface indicating that the dynamics of dipole transitions has changed to the $[1\bar{1}0]$ direction. To highlight this important point we have resolved the total SDA of CO/Cu(110) into the separate contributions of surface-to-surface (*ss*), bulk-to-bulk (*bb*), bulk-to-surface (*bs*), and surface-to-bulk (*sb*) optical transitions with the same criteria adopted for the clean surface [11]. We find that at low energy *ss* transitions represent the main contribution to the total SDA and they are excited by light along the $[1\bar{1}0]$ direction since $\Delta\epsilon > 0$. Moreover, also *sb* and *bs* transitions, giving rise to the positive $\Delta\epsilon$ shoulder between 2 and 3.5 eV, follow the same dynamics. The further analysis of the separate SDA contributions of the surface and subsurface Cu layers, shown in Fig. 2, indicates that the different SDA sign between the clean (see inset) and the CO covered surface originates from surface states localized at the Cu surface layer.

The existence of surface states peculiar of reconstructed CO/Cu(110) will be now exploited to model the kinetics of the CO absorption, monitored in the RAS measurements [7] by Sun *et al.*, through the behavior of the intensity $I(\theta)$ of the 2.2 eV peak vs coverage θ. A careful inspection of $I(\theta)$ for 15 different CO coverages (see Fig. 1 in Ref. [7]) led us to hypothesize three regimes in the optical response vs coverage: (I) the early regime (*impurity regime*) where the peak value $I(\theta)$ decreases much faster than linearly with θ, keeping the same feature of the clean surface; (II) the intermediate regime where the peak turns to a flat curve; (III) the ordered regime where $I(\theta)$ becomes negative assuming eventually the features of the reconstructed surface.

The *impurity regime* is ascribed to the progressive suppression of Cu surface states due to their loss of quantum mechanical coherence in the presence of a CO molecule. This acts as an impurity whose effective cross

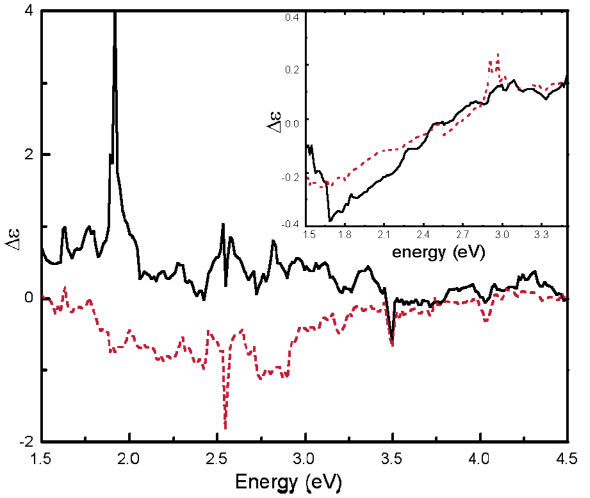

FIG. 2 (color online). Calculated SDA of the Cu surface (solid) and subsurface (dashed) layers in CO/Cu(110). Inset: the same in clean Cu(110).

section A is much larger than the physical dimension of the molecule itself. It is argued [7] that "the surface optical transitions are quenched" over A ("quenching area") leading to a steep reduction of $I(\theta)$ at very low coverage. In our model we mimic the loss of coherence of the metallic surface states by the elimination of the ss transitions in the RA of the clean surface. We further assume $I(\theta)$ to be proportional to an effective coverage depending on the effective CO cross section A. Finally, we picture the latter two regimes as the coexistence of quenching areas and "coherence domains," where CO induced surface states increase with θ, at expenses of the quenching areas until final reconstruction. In light of our results we can evaluate the parameters of the model. Let us consider the intensity value of the RA peak $I(\theta)$ (from I_0 to I_{CO}, see Fig. 1) in the different regimes and let θ_A be the coverage at the passage between regimes I and II. To estimate θ_A, we assume that the width ΔE of the RA peak I_0 gives us the order of magnitude of the effective cross section $A = \pi(\Delta x)^2$ since $\Delta x = [(\Delta E/\hbar)\sqrt{2m/E}]^{-1} \simeq 14$ Å. We have taken $\Delta E = 0.2$ eV. We get $A \simeq 600$ Å^2 corresponding to one CO molecule every $N_A = 33$ (2×1) unit cells and yielding a coverage $\theta_A = 0.031$ ML, with 1 ML = 1 CO molecule per (2×1) unit cell. Subtracting the ss contribution from the RA of the clean surface we get RA$_{\mathrm{imp}}$ plotted in Fig. 3 (top) that shows a peak intensity drop >50% compared to I_0. We denote henceforth by I_{ss} the peak intensity of the ss only RA (not shown). With $\theta_A = 0.031$ ML (equivalent to 0.0527 L [1 langmuir (L) $= 10^{-6}$ Torr s] since 1 ML = 1.7 L in Ref. [7]) we obtain about the same steep reduction of intensity observed in the experiments at a coverage equal to 0.059 L. θ_A and the other parameters evaluated above allow us to describe the behavior of the intensity $I_1(\theta)$ for $0 < \theta < \theta_A$ (impurity regime) and $I_2(\theta)$ for $\theta_A < \theta < 1$ (second and third regimes), reported in Fig. 3 (bottom) and obtained according to the following relations: $I_1(\theta) = I_0 - (\theta/\theta_A)I_{ss}$ and $I_2(\theta) = [I_{\mathrm{imp}}(1-\theta) + I_{\mathrm{CO}}(\theta - \theta_A)]/(1-\theta_A)$, where $I_0 = 0.024$, $I_{\mathrm{CO}} = -0.025$, $I_{ss} = 0.015$, and $I_{\mathrm{imp}} = 0.009$ are taken from our calculations (see Figs. 1 and 3). I_1 and I_2 are normalized to the respective coverage ranges. We notice that in $I_1(\theta)$ the parameter θ_A enhances the actual coverage θ by a factor $\simeq 30$ close to the value estimated experimentally [7]. We locate the intermediate regime in the region of $I_2 > 0$ by observing that I_2 vanishes for $\theta = 0.29$ ML corresponding to 0.493 L, a value close to that of 0.505 L at which, in agreement with Fig. 1 of Ref. [7] (see 11th curve from top in the inset), we have placed the onset of the final, linear regime. We can now bring the representation of the impurity regime into closer resemblance to the experimental data [7] by observing that $I_1(\theta)$ is just the linear approximation of the exponential curve $I_3(\theta)$ in Fig. 3, at vanishing θ. We remark that $I_2(\theta)$ intersects $I_3(\theta)$ for θ within the range assigned to the intermediate

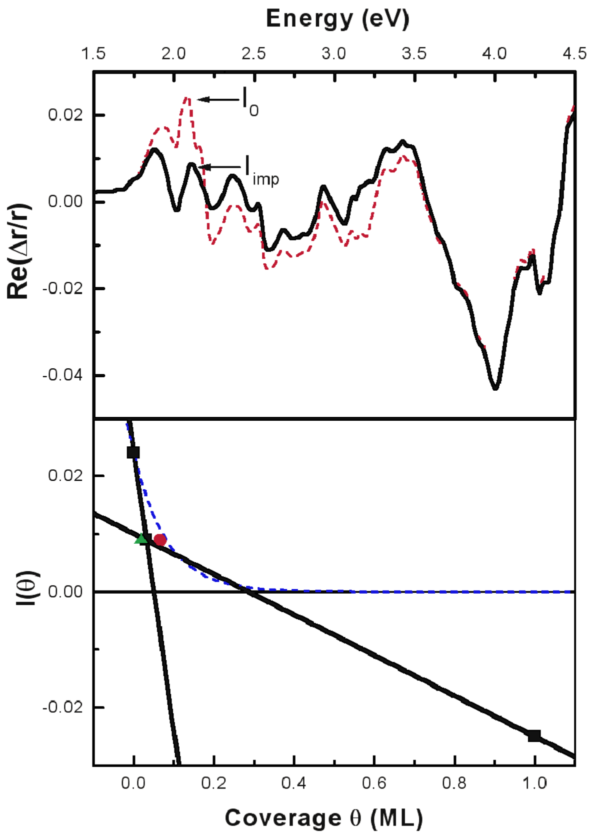

FIG. 3 (color online). Top: calculated reflectance anisotropy spectrum RA$_{\mathrm{imp}}$ (solid) compared to the total RA of Cu(110). Bottom: calculated intensity of the RA peak $I(\theta)$ at different CO coverages. Straight lines with full squares represent I_1 and I_2 with θ_A given in the text. Full circles and triangles denote θ_A values obtained with [7] $A = 1000$ Å^2 and $\Delta E = 0.3$ eV, respectively (see text). The dashed curve is $I_3(\theta) = I_0 e^{-[(\theta\, I_{ss}/I_0)/\theta_A]}$.

regime where the exponential decay $I_3(\theta)$ alone cannot represent the complex mechanism described at point II of our model. We have checked the soundness of the above conclusions against different, reasonable choices of the key parameter A determining θ_A. If we take $A = 1000$ Å^2 (from Ref. [7]) or $A = 280$ Å^2 (from $\Delta E = 0.3$ eV) we get θ_A equal to 0.066 and 0.018 ML, respectively. These new values shift slightly θ_A without affecting significantly the passage from regimes II to III, as shown in the bottom panel of Fig. 3.

Although the present findings apply strictly to CO/Cu(110), we feel to compare also with different adsorbates. Experimental studies of 3-thyophene carboxilate [5] and 9-anthracene carboxylic acid [6] on Cu(110) show the evolution of the 2 eV RA peak upon coverage, from the clean surface to the $p(2 \times 1)$, similar to that of CO/Cu(110) described here. Previously, a very exhaustive photoemission study on H/Cu(110) [13] showed that the progressive quenching of surface states intensity upon coverage is nonlinear, as proposed for CO/Cu(110). On the other hand, Jin *et al.* [10] observed a linear behavior in the RA evolution with coverage in different thermal conditions. Comparing carefully the experimental conditions of all these systems, the importance of investigating the role of annealing comes out.

In conclusion, we have calculated *ab initio* the reflectance anisotropy of CO/Cu(110)-$p(2 \times 1)$ and found its features to be in very good agreement with the experiments. We have identified the signature of the CO adsorbate at the $p(2 \times 1)$ reconstruction in the negative peak at low energy and proved it to be due to surface state transitions peculiar of the CO covered surface and localized in the two first Cu layers. These determine the change in the light absorption direction demonstrated by the sign reversal of relevant RA and SDA structures with respect to that of the clean surface. The above findings have led us to devise a quantitative model, in the whole coverage range, for the kinetics of the CO adsorption, whose critical parameters are consistent with the experimental ones. We close by hoping that new structural measurements at several intermediate coverages bring to light the existence of regions with different reconstructions. This would help to confirm further, by additional calculations, the picture underlying our present model.

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