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Chemisorption-induced changes of the surface dielectric function for W(110)

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The change in reflectance due to adsorption of H_2, O_2, and CO on W(110) was measured for photon energies in the range 0.5 to 6.0 eV. The changes in dielectric function and joint density of states were obtained and analyzed in terms of vertical transitions in the projected band structure of the W(110) surface Brillouin zone. A new surface resonance is found above the Fermi level.

I. INTRODUCTION

In the past decade many different techniques have been applied to the study of chemisorption of gases on transition-metal surfaces. Among them are ultraviolet photoemission (UPS),[1-3] field emission (FE),[4,5] and ion-neutralization (INS)[6] spectroscopies. Such studies mainly provide information about the density of filled electronic states near the surface.

Surface-reflectance spectroscopy (SRS) has emerged in recent years as a promising tool which complements photoemission for the investigation of metal surfaces with chemisorbed gases. Experimental studies, at both near-normal and oblique incidence, have been reported for H_2, O_2, N_2, and CO chemisorbed on Mo(100),[7] Ni(111),[8] W(100),[9,10] and W(111).[11]

SRS is a very sensitive optical technique for measuring the small changes in reflectance, $\Delta R(\omega)/R(\omega)$, ($\lesssim 1\%$) that occur when (sub)monolayer(s) of atoms or molecules are chemisorbed on an atomically clean surface in ultrahigh vacuum. The presence of the adsorbate modifies the electronic contribution made by the surface region causing a change in reflectivity.

SRS studies give two kinds of information about the chemisorption process. An understanding of the relative energy position of initial and final electronic states is obtained by studying the energy dependence of $\Delta R/R$ at fixed coverage. Also, the study of the coverage dependence of $\Delta R/R$ at fixed photon energy allows a determination of the coverage at which different adsorbate binding states are being filled.

We report here SRS studies of several gases (H_2, CO, and O_2) chemisorbed on W(110). A considerable amount of work has been done on W(110) with various techniques. Angle-resolved photoemission studies[12] have identified specific surface contributions in the photon energy range where bulk contributions are not possible due to a conduction-band gap.

We report here the changes in dielectric functions induced by different adsorbates, interpret their peaks in terms of interband transitions, and identify both initial and final electronic states.

In most of the previous SRS studies the change in the surface dielectric function was obtained by fitting the dielectric function to a sum of Lorentzian oscillators.[7,9,11] The energy of each oscillator was then compared to the position of those peaks observed in photoemission. Good correlation encouraged identification of the energies of the Lorentizian oscillators as those of the adsorbate levels and surface states. On the other hand, we consider the optical transitions excitation energies to be those of the peaks in the change in dielectric function and view the fitting just as a mathematical procedure. This work attempts to interpret the change in dielectric response upon adsorption in terms of direct optical transitions between surface bands in the projected band structure of the (110) surface Brillouin zone (SBZ).

II. EXPERIMENT

Because chemisorption-induced changes of reflectance are small, an instrumental stability of one part in 10^4 is necessary to measure the 1% change to one part in 100. This was obtained using the double beam spectrometer shown in Figure 1.

The sample is a thin ribbon of tungsten ($13 \times 3 \times 0.1$ mm^3) with its surface oriented to within 0.5° of the (110) crystal plane. An atomically clean surface was obtained by procedures found to be adequate by Auger measurements. The sample was resistively heated to 2200 °C for a short time and periodically heated in oxygen to eliminate residual carbon contamination.

The sample chamber was maintained at a background pressure of 2×10^{-10} Torr at which it would take about 10 min to build 1/10 of a monolayer on the surface. Various gases were admitted into the chamber through leak valves and their pressure was monitored with a partial pressure analyzer.

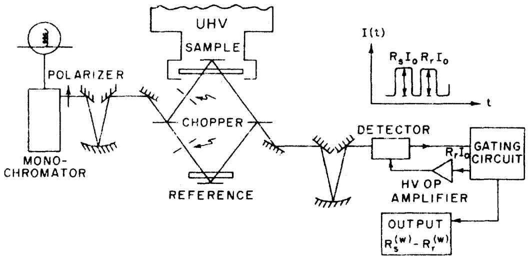

FIG. 1. Schematic diagram of the experimental system.

Unpolarized light from a halogen-tungsten ($\hbar\omega \leq 4.8$ eV), or a low-pressure deuterium discharge lamp ($4.5 \leq \hbar\omega \leq 6.0$ eV), was passed through a prism monochromator and polarizer to select wavelength and *s* polarization (Fig. 1). The light beam enters an optical box consisting of CaF_2 aluminum coated mirrors and 50% transmission beam splitters. It is divided into two beams, one of which enters the ultra-high vacuum chamber at 41° angle of incidence and is reflected at the same angle, from a reference sample placed inside the optical box.[13] The spherical mirrors focus the beams on the samples within a 2-mm-diameter spot. Differences in optical path were kept to a minimum to reduce instabilities as the phonon energy was varied.

Both reference and sample beams are chopped at 150 Hz by a pair of tuning forks approximately 180° out of phase. In this configuration the periodic photomultiplier signals are alternatively the reference (R_rI_0), sample (R_sI_0), and dark current intensities. The output of the photomultiplier corresponding to the signal from the reference sample is controlled by a feedback mechanism that adjusts the photomultiplier gain to keep the reference signal voltage constant (1 V).[14] We were able to detect reflectivity changes of 0.6×10^{-4} with a lead sulfide infrared detector for $\hbar\omega \leq 1.5$ eV, and 0.2×10^{-4} with photomultipliers in the visible and near-uv regions.

The normalized change of reflectance from the clean W(110) sample and the reference sample were measured continuously as a function of photon energy. The difference between these two signals was recorded in a multichannel analzyer (MCA). After the measurement was completed, gas was admitted into the chamber until a monolayer of it was chemisorbed on the sample. By repeating the above procedure the difference between the chemisorbed and reference sample signals was measured in the same energy range and recorded in a different channel of the MCA.[15] The former difference was digitally subtracted from the latter and the normalized change of reflectance for *s*-polarized light $\Delta R_s/R_s$ was obtained.

Further reduction of the noise level and increase in stability was accomplished by statistical averaging of the data eight to sixteen times. The uncertainty in the data due to differences from run to run was reduced in this way by a factor of 4.

III. RESULTS

Figure 2 shows the resulting spectral curves $\Delta R_s/R_s$, for saturation coverage of H_2, O_2, and CO chemisorbed on W(110). It is convenient to consider separately three different energy regions in the change of reflectivity spectra: near infrared ($0.6\text{ eV} \leq \hbar\omega \leq 1.5$ eV), visible and near ultraviolet ($1.5\text{ eV} \leq \hbar\omega \leq 4.8$ eV, and ultraviolet ($4.8\text{ eV} \leq \hbar\omega \leq 6.0$ eV).

In the near infrared region, a rapidly varying structure is seen for all the adsorbates although with different relative strengths (Fig. 2). Experiments done in the same spectral region with unpolarized light revealed that the structure remains unchanged for hydrogen adsorption. On the other hand, the structure disappears in the presence of O_2 and CO and $\Delta R/R$ shows instead a minimum at 1.2 eV (Fig. 3).

This behavior is remarkably different from that of the other two low-index faces of tungsten already studied. $\Delta R_s/R_s$ decays very rapidly from positive to negative values on the (100) face for all gases adsorbed[9] because of the quenching of the surface state at −0.3 eV. There is an adsorbate-independent positive peak at 1.0 eV for the (111) face.[11]

In the photon energy range above 1.5 eV, very similar structure appeared in $\Delta R_s/R_s$ for oxygen and carbon monoxide adsorption because there are no adsorbate levels present in this region (Fig. 2). For both gases the reflectivity spectra show two peaks at 2.1 and 3.7 eV, respectively, of 0.6 eV

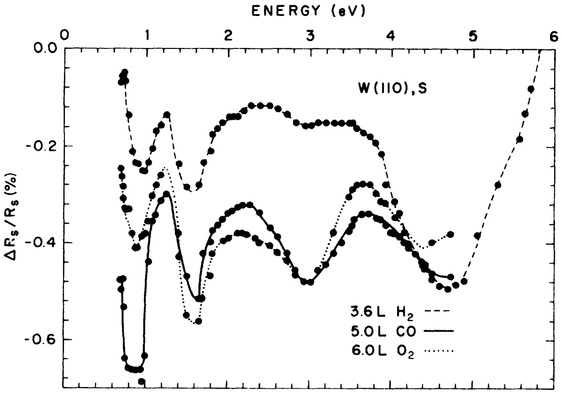

FIG. 2. Dependence of the normalized change of reflectance $\Delta R_s(\omega)/R_s(\omega)$ on photon energy for saturation exposures of H, CO, and O on W(110).

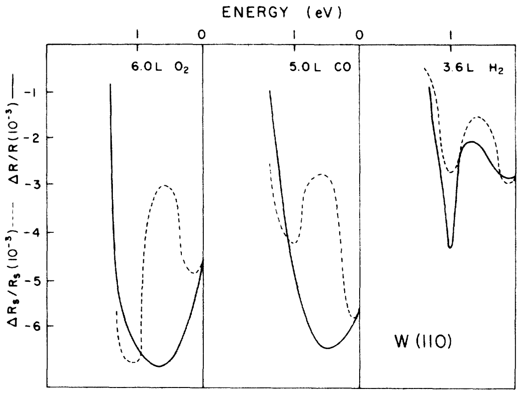

FIG. 3. Normalized change of reflectance in the near-infrared photon-energy region for s-polarized (full line) and unpolarized (dashed line) light.

half width. The similarities in $\Delta R_s/R_s$ for oxygen and carbon monoxide adsorption were also present for the other two low-index faces of tungsten.[9,11] On the other hand, no distinct features appeared in the hydrogen spectrum up to 3.4 eV, and for higher energies it consistently decreases to a minimum at 4.8 eV.

The effect of hydrogen was studied in the ultraviolet region up to 6.0 eV. In this energy range ($4.5\ \mathrm{eV} \leq \hbar\omega \leq 6.0\ \mathrm{eV}$) the experiments were performed at near normal incidence because of the poor transmission of the available polariods. The experimental data in the ultraviolet and visible regions were matched in the overlap region through a simple mathematical relation. A weighting factor took into account the changes in angle of incidence and electric field, as well as the effects of anisotropies. This approach did not succeed for oxygen and carbon monoxide adsorption. Due to directionality of the adsorbate bonds $\Delta R_s/R_s(\omega, \phi)$ exhibits extra structure as a function of the azimuthal angle. We found no simple mathematical relation between $\Delta R_s/R$ for unpolarized light and $\Delta R_s/R_s(\omega, \phi = 0)$ as in the case of hydrogen,[15] A detailed study of the W(110) anisotropy will be published elsewhere.

An analysis of $\Delta R_s/R_s$ requires a dielectric model to relate the observed reflectance changes to the chemisorption-induced changes of the electonic structure at the surface. We adopt the classical model of McIntyre and Aspnes (MA), in which the vacuum-metal system is treated as three phases: substrate, surface, and vacuum. This model represents a reasonably good approximation because the short screening length of electrons in a metal guarantees that the change in electronic structure does not extend beyond two or three layers.[16,17] Therefore, the reflectivity changes are due mainly to changes in the surface electronic structure.

Within this model the surface region is treated as an isotropic, uniform layer of thickness d ($d \ll \lambda$, wavelength of the light). A complex dielectric function characterizes the surface ($\epsilon_s = \epsilon_{1s} + i\epsilon_{2s}$). The bulk complex dielectric function is $\epsilon_b = \epsilon_{1b} + i\epsilon_{2b}$. $\Delta R_s/R_s$ for chemisorption-induced changes and s-polarized light becomes[18]

$$\frac{\Delta R_s}{R_s} = \frac{-8\pi d}{\lambda}\cos\theta\left(\frac{\epsilon_2 b}{(1-\epsilon_1 b)^2 + \epsilon_2 b^2}\Delta\epsilon_1 + \frac{(1-\epsilon_1 b)}{(1-\epsilon_1 b)^2 + \epsilon_2 b^2}\Delta\epsilon_2\right). \tag{1}$$

This equation relates the relative reflectance differences to changes in an average, effective complex surface dielectric function $\Delta\epsilon_s = \Delta\epsilon_1 + i\Delta\epsilon_2$.

It can be shown that the MA formula holds for each of the principal axes of the dielectric tensor on the plane of the sample.[15] Therefore, our dielectric functions refer to adsorption due to an electric field in the $\langle 1\bar{1}0\rangle$ direction. The assumption of a local dielectric response was already discussed by Feibelman[19] in terms of a microscopic nonlocal dielectric function, and his results were equivalent to MA's, due to the slow variation of the electric field across the surface region for s-polarized light. However, for p-polarized light a nonlocal theory may be necessary.[20] Since only $\Delta R_s/R_s$ is measured, the two unknowns $\Delta\epsilon_1$ and $\Delta\epsilon_2$ cannot be determined directly from Eq. (1). Therefore, we represent $\Delta\epsilon_s$ as a sum of Lorentzians, whose parameters are computer adjusted to reproduce the experimental spectra.[7-11]

Different groups of oscillator parameters were found that reproduce the data equally well and give essentially the same dielectric functions. Therefore, the energies of the oscillators should not be identified as the energies of important optical transitions, since the oscillator parameters are not uniquely determined. The transition energies are instead obtained from the peaks of $\Delta\epsilon_2$. Figure 4 shows the surface dielectric response for H_2, CO, and O_2 adsorption. These were obtained considering $\Delta\epsilon_s$ a sum of five Lorentzians.

The change in joint density of states, $\Delta J_{if}(\omega)$, was calculated considering constant dipole matrix elements, $\Delta J_{if}(\omega) = \omega^2 \times \Delta\epsilon_2(\omega)$. The resulting spectral curve is shown in Fig. 5 for H_2, O_2, and CO adsorption. An interpretation of these results is presented in the following section.

IV. DISCUSSION

Christensen and Feuerbacher[2] calculated the band structure of tungsten using the relativistic-augmented-plane-wave method. The crystal potential, constructed by superimposing atomic poten-

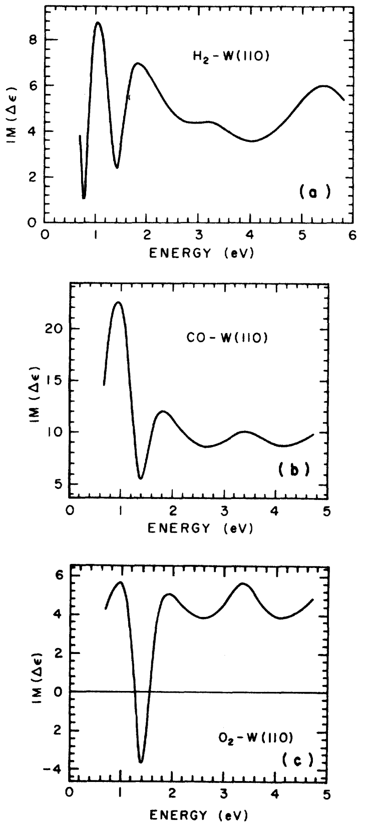

FIG. 4. Spectra of changes in the imaginary part of the surface dielectric function caused by (a) hydrogen, (b) carbon monoxide, and (c) oxygen chemisorption at room temperature.

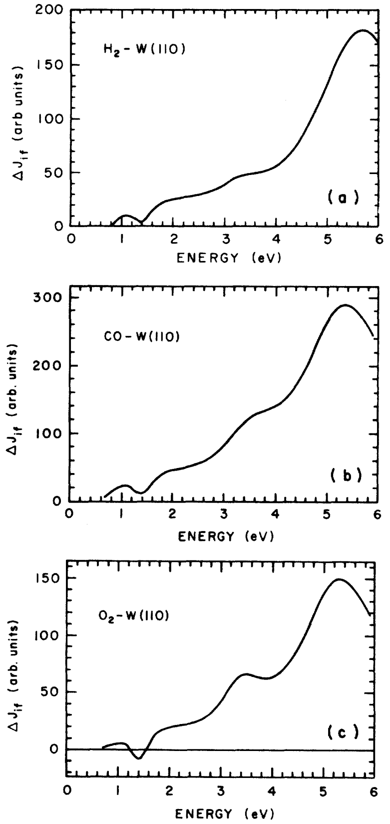

FIG. 5. W(110) changes of the joint density of states $\Delta J_{if} = \omega^2 \times \Delta\epsilon_2(\omega)$ upon: (a) hydrogen, (b) carbon monoxide, and (c) oxygen chemisorption as a function of photon energy.

tials and charge densities, was optimized by means of a comparison to optical absorption, photoemission spectra, and Fermi surface measurements.

The surface-band structure, shown in Fig. 6, was obtained by projecting Christensen and Feuerbacher's calculated band structure onto the (110) two-dimensional surface Brillouin zone. This projected band structure (PBS) refers only to eigenvalues of Bloch-type states because their calculation did not take into account wave functions localized at the surface. Therefore, the corresponding eigenvalues, which are surface states and resonances, are not obtained in the (110) PBS. As shown by theoretical calculations,[19,20] surface states and resonances exist mainly in gaps and regions of low electronic density of states. Their position in the PBS can be inferred knowing the density of filled electronic states and the excitation energy of the electronic transition from UPS and SRS, respectively. $\Delta\epsilon_2$ shows three adsorbate-independent peaks (Fig. 4) at energies at which the bulk dielectric function $\epsilon_{2b}(\omega)$ also has peaks.[21]

On the other hand, surface structure (such as the 1.4 eV dip) shows sharper features than the bulk-like peaks, reflecting the small dispersion of both initial and final electronic states. The 1.4 eV dip in $\Delta\epsilon_2$ is attributed to the quenching of a surface

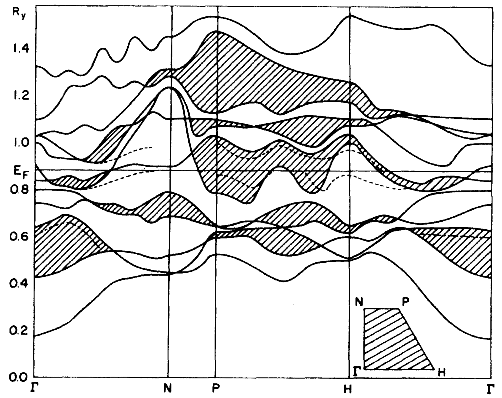

FIG. 6. Projected band structure for W(110) surface. Dashed regions refer to energy gaps. Full lines represent the edges of the different bands and dashed ones refer to the surface resonances. The dot-dashed lines along ΓN and ΓH are the H adsorbate level. $\frac{1}{4}$ of the BZ is shown in the right-hand corner of this figure.

resonance. The initial state of this transition has been determined from UPS experiments. Angle-resolved-photoemission studies located such structure at −1.30 eV with respect to E_F,[22] and wide-collection-angle (45°) experiments at −1.47 eV from the Fermi level.[23] This state appeared at about the same energy in both studies. However, the information obtained in the two cases referred to contributions from different regions of the BZ.

The quenching of the W(110) resonance under discussion is not as drastic[9] if the electric field is along the $\langle 1\bar{1}0\rangle$ direction, but it shows stronger quenching for an electric field in the $\langle 001\rangle$ direction.[15] Recent angle-resolved-photoemission experiments[24] showed that this surface resonance exists practically over the whole BZ. Its location along the principal directions on the (110) PBS is shown in Fig. 6. Considering them as the initial states of the transition and given an SRS excitation energy of 1.4 eV, we show a possible set of final states above E_F (Fig. 6). These final states are located in the gap as well as in low electronic density regions. Therefore, we suggest that a surface resonance exists above E_F breaking from the gap between bands 3 and 4.

As already mentioned, $\Delta\epsilon_2$ exhibits peaks at 1.0, 1.8, and 3.3 eV for the three adsorbates. These peaks appear also in the imaginary part of the bulk dielectric function. In analogy to the analysis of the bulk data, each peak can be associated with transitions between specific pairs of bands. The peak at 1.0 eV in $\Delta\epsilon_2$ is due to transitions between pairs of bands (3,4) and (4,5) (in the notation of Ref. 2). The structure at 1.8 eV is due to a large number of transitions between bands 4 and 5 and the major contribution to the peak at 3.3 eV comes from (3,4) transitions. Christensen and Feuerbacher's calculation shows two van Hove singularities in the joint density of states (J_{34}). The one at 3.3 eV is related to parallel-band transitions along the ΓN direction.

As a possible explanation of why $\Delta\epsilon_2$ peaks exist at the same energy as ϵ_{2b} ones,[21] we may assume that there are no core bands contributions to the change of the dielectric function and that most of the adsorbate levels are located outside our region of measurement. Under those conditions a decrease in the oscillator strength corresponding to a given transition originates from an increase in the oscillator strength associated with other transitions. The presence of a surface introduces sharp structure, such as surface states and resonances, that can exist throughout the whole two-dimensional Brillouin zone.[16,17] Some new optical transitions are allowed among them with some transition probability. Therefore, a decrease in the oscillator strength corresponding to pairs of bulk-like bands could be caused by an increase in the oscillator strength associated with transitions among both surface resonances. However, when chemisorption takes place the process reverts: A number of surface states or resonances are quenched reducing the oscillator strength corresponding to those transitions and restoring it to transitions between pairs of bulk-like bands. Therefore, when the chemisorbed and clean dielectric functions are subtracted, some peaks will remain at the same energy as that in ϵ_{2b}.

Saturated adsorption of CO on W(110) at room temperature[23,25] leads to an adsorbed layer composed primarily of virgin CO[23]. These virgin peaks were observed in UPS experiments at 7.0 and 11.0 eV below the Fermi level. Therefore, the contributions of virgin CO are located well outside the energy region considered in this work. A residual β state was observed in UPS room-temperature experiments at −0.7 eV with respect to the Fermi level.[23] The 1.0 eV peak in $\Delta\epsilon_2$ [Fig. 4(b)] is considerably larger for CO adsorption than for hydrogen or oxygen adsorption. Their normalized relative strengths are 4 to 1.5 to 1, respectively. Therefore, we considered the SRS peak at 1.0 eV as caused by transitions between the β state and band 3, to states located in band 4 at about 0.3 eV above E_F.

The main features caused by oxygen adsorption observed in UPS experiments are[26] a peak at 6.0 eV below E_F outside the energy range we considered, and a shoulder at 2.0 eV. The latter one can be associated with the peak of $\Delta\epsilon_2$ [Fig. 4(a)] at 1.8 eV. Therefore, an adsorbate level could be located at 1.8 eV with respect to E_F and the corresponding final state at 0.2 eV above the Fermi level. We conclude that the main effect of CO and O_2 adsorption in this energy range is to alter the relative strength of bulk-like transitions.

The chemisorption of hydrogen on W(110) has not been investigated as extensively as hydrogen on W(100). As with the W(110) surface, thermal desorption of a saturated hydrogen layer on W(110) produces two peaks, β_1 and β_2, supposedly associated with two different binding configurations of the adsorbate. Feuerbacher and Fitton's photoemission experiments[27] revealed to main peaks: The one at −2.8 eV was dominant at low coverage, whereas at high coverage a −4.0 eV peak was dominant. Plummer *et al.* found[23] those peaks at −2.2, −3.9, and a new peak at −6.5 eV. The differences between them probably originate from their use of a different photon energy and collection angle. The bulk dielectric functions shows a peak at 5.2 eV.[21] The same structure appears in $\Delta\epsilon_2$ shifted towards higher energies [Fig. 4(a)]. This change in excitation energy upon hydrogen adsorption can be due to a strong interaction between an adsorbate level and a surface band. As a result, the initial state of the transition is shifted towards lower energy and the $\Delta\epsilon_2$ peak to higher energies. Therefore, the 5.6 eV peak originates from a large number of transitions between a combination of band 2 and the -4.0 eV adsorbate level to band 5. The -4.0 eV adsorbate level probably follows the conduction band edge at least in the ΓN, ΓH directions (Fig. 6), since the photon energy is insufficient to obtain contributions from the other principal directions in the PBS.

We could not observe any peak in $\Delta\epsilon_2$ associated with the low coverage β state. This indicates a relatively small dipole matrix element associated with the transition for an electric field in the $\langle 1\bar{1}0\rangle$ direction on the plane of the sample. However, with an electric field in the $\langle 001\rangle$ direction, there is strong adsorption at 2.6 eV associated with the low-coverage β state.[15] Therefore, our results indicate that both β states coexist at saturation and that the dipole matrix elements are varying strongly with the azimuthal angle of the electric field. This reflects the directionality of the wave functions involved in the electronic transitions.

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