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Photodesorption of CO from Si(100)-2 × 1: wavelength and intensity dependence

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Abstract

The adsorption of CO on Si(100)-2 × 1 has been studied and characterized by temperature programmed desorption spectroscopy and electron energy loss spectroscopy. Furthermore, the relative CO photo-induced desorption yield has been measured as a function of photon intensity and wavelength, from the visible to the near-UV. The results suggest that a substrate mediated mechanism involving photogenerated carriers is responsible for the photodesorption.

Keywords: Carbon monoxide; Low index single crystal surfaces; Photon stimulated desorption; Platinum; Surface photochemistry

1. Introduction

There have been many studies conducted to investigate the interaction of CO with metal surfaces. However, the study of CO adsorption on semiconductor surfaces has been limited, and the mechanisms involved in CO–semiconductor interactions are poorly understood. It has long been established that CO does not adsorb on a clean Si(111)-7 × 7 surface at temperatures above 77 K [1]. Recently it was reported by Bu and Lin that CO adsorbs molecularly on a Si(100)-2 × 1 surface at 100 K with a high sticking coefficient [2]. In addition, they found that a near monolayer of CO was almost entirely photodesorbed when the CO/Si(100)-2 × 1 system was irradiated with 308 nm excimer laser radiation for 2 min. No further photodesorption studies were reported and the photodesorption cross-section was not

determined. It can be concluded, however, from the data presented that CO/Si(100)-2 × 1 has a significant photodesorption cross section.

Due to the band structure of semiconductors, their optical properties have more variations in wavelength in the 200–800 nm range than those of metals. For substrate mediated photodesorption mechanisms, these variations will be reflected in the photoyield. A photochemical system of molecules adsorbed on a semiconductor that has been studied in detail is NO/Si(111)-7 × 7 [3–8]. However, the analysis is complicated as NO adsorbs on Si(111)-7 × 7 in part molecularly and in part dissociatively at temperatures above 77 K, resulting in four adsorbed species: N, O, NO and N₂O. Furthermore, the photoyield of NO/Si(111)-7 × 7 involves three product species: NO, N₂O and N₂. In contrast, CO does not dissociate upon adsorption on Si(100)-2 × 1 and it desorbs molecularly as well. This property of CO, along with the propensity of CO to photodesorb from Si(100)-2 × 1, makes the study of the CO/Si(100)-2

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$\times 1$ system ideal for providing insight into the photochemical desorption mechanisms of molecules from semiconductors.

In this work, temperature programmed desorption (TPD) and electron energy loss spectroscopy (EELS) were initially utilized to study and characterize CO interaction with Si(100)- 2×1 . Subsequently, a series of photo-induced desorption investigations was carried out, resulting in a measurement of the radiation intensity dependence of the photoyield and a detailed measurement of the wavelength dependence of the photoyield and photodesorption cross section.

2. Experimental procedures

The thermal desorption and photodesorption experiments were performed in a UHV system with a base pressure of $< 1 \times 10^{-10}$ Torr. Both the UHV system and the optics arrangement used for the photodesorption experiments are described in detail elsewhere [9–12]. The $1 \text{ cm} \times 2 \text{ cm}$ sample was cut from a single crystal n-type Si(100) wafer with a resistivity of $3.9 \Omega \cdot \text{cm}$. The sample was cleaned with ~ 20 cycles of Ne^+ sputtering (500 eV for 10 min at $7 \mu\text{A}$) while held at 85 K, followed by annealing (980 K for 10 min) and then a $< 2 \text{ K/s}$ temperature ramp down to 85 K. After the initial series of cleaning cycles, the surface structure was checked with LEED; the integral and half order spots associated with the 2×1 surface appeared sharp and bright. Auger electron spectroscopy and EELS (Fig. 2) were used to check the cleanliness of the Si surface after undergoing similar cleaning procedures. The sample was dosed with $^{31}\text{C}^{18}\text{O}$ (Isotec) through background exposure from a non-directional doser.

The sample was mounted to a LN_2 cooled dewar-type manipulator which allowed for sample cooling to a base temperature of 85 K. An $\sim 200 \text{ \AA}$ thick Ta film was deposited on the back of the Si sample. The sample was clipped to Ta foil, which was in turn spot-welded to the Ta sample mount posts of the manipulator, allowing for resistive heating of the sample. The sample thermometry was done through chromel/alumel thermocouple pairs spot-welded to Ta clipped to the sample.

A 1000 W Hg–Xe arc lamp system was used as the photon source for the photodesorption experi-

ments. For all of the photodesorption experiments conducted, a specific incident photon wavelength was selected by passing the collimated arc lamp beam (1 cm diameter) through narrow band interference filters (made by Oriel and Ealing) with bandwidths of 10–11 nm. The first photodesorption experiments investigated the general behavior of the photodesorption decay curve as a function of $^{31}\text{C}^{18}\text{O}$ dose at 85 K using 313 nm photons to irradiate the sample. Using these data, a constant $^{31}\text{C}^{18}\text{O}$ exposure was chosen for the photodesorption wavelength dependence measurements. For the intensity dependence measurements, 313 nm photons were used; this particular wavelength was chosen because it was a relatively strong emission line of the arc lamp and produced a significant photodesorption yield curve with very little noise. The lamp intensity was controlled by attenuating the beam with neutral density filters and monitored with a thermopile detector. All the photon experiments were performed with unpolarized light incident on the sample at 45° from the surface normal. Sample irradiation was controlled by a manually operated shutter placed in the lamp beam path.

The $^{13}\text{C}^{18}\text{O}$ desorbed molecules from both the TPD and photodesorption experiments were detected by monitoring the $m/e = 31$ signal with a UTI 100C quadrupole mass spectrometer. The sample and the spectrometer were situated such that the spectrometer axis was normal to the sample surface. The mass spectrometer nose cone was positioned $\sim 2 \text{ mm}$ from the sample and was aimed at the center of the sample. The sample heating and cooling, and the mass spectrometer were controlled by a personal computer through a CAMAC crate [10].

The EELS was performed in a separate chamber [13] with a differentially pumped spectrometer equipped with a double-pass monochromator and single-pass analyzer. The incident electron energy was 10 eV, with both the incident and collection angles 60° from the sample normal.

3. Results

3.1. TPD

To verify the adsorption of CO on Si(100)- 2×1 , TPD was performed for varying exposures of $^{31}\text{C}^{18}\text{O}$,

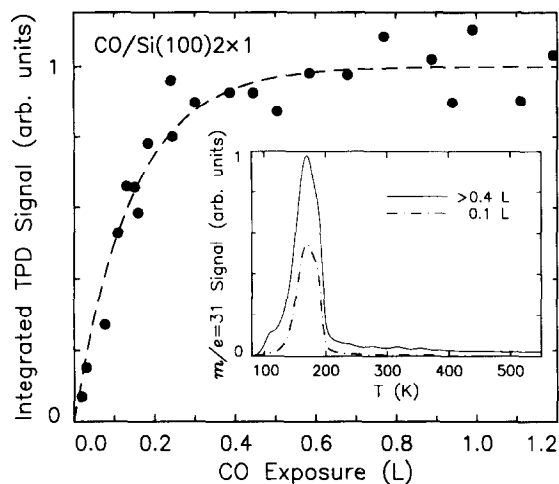


Fig. 1. The $m/e = 31$ temperature programmed desorption signal as a function of adsorbate exposure for $^{13}\text{C}^{18}\text{O}$ desorbing from $\text{Si}(100)\text{-}2\times 1$. For each background $^{13}\text{C}^{18}\text{O}$ exposure, the area under the TPD peak centered at 170 K was integrated. The dashed line is the best fit to the data using Eq. (2). Inset: two TPD spectra after low and high $^{13}\text{C}^{18}\text{O}$ exposures. At an exposure of 0.25 L, a shoulder on the lower temperature side of the peak begins to appear, which grows with increasing $^{13}\text{C}^{18}\text{O}$ exposure until about 0.4 L, a coverage above which the spectra change very little. All exposures were performed at a sample temperature of 85 K. The heating rate was 2 K/s.

which was used to avoid $^{12}\text{C}^{16}\text{O}$ and $^{14}\text{N}_2$ background signals. Two typical TPD spectra at low and high exposures of 31 initially adsorbed at 85 K are shown in the inset of Fig. 1. At low dosages, a single peak at 171 ± 2 K was observed in the $m/e = 31$ signal. As the 31 exposure was increased, the peak became slightly broader; a shoulder at lower temperatures emerged at an exposure of 0.24 L (1 langmuir (L) = 10^{-6} Torr · s) and became more prominent for higher doses. This low-temperature shoulder could be an indication of another weakly adsorbed CO state or a coverage effect. These results are consistent with previously published $\text{CO}/\text{Si}(100)\text{-}2\times 1$ results in which a thermal desorption peak of 180 K for ^{13}CO was reported and higher coverages resulted in the population of more weakly bound states [2].

A curve showing the integrated area under the main TPD peak as a function of $^{13}\text{C}^{18}\text{O}$ exposure is presented in the main body of Fig. 1. Assuming langmuir adsorption, the sticking coefficient for CO on $\text{Si}(100)\text{-}2\times 1$ can be expressed as

$$S = S_0(1 - \theta), \quad (1)$$

where θ is the adsorbate coverage normalized to the saturation coverage and S_0 is the sticking coefficient for a clean surface ($\theta = 0$). The total coverage dependence on the exposure can then be expressed as

$$\theta(t) \propto 1 - e^{-\beta \varepsilon}, \quad (2)$$

where ε is the adsorbate exposure (in units of L) and β is a constant (L^{-1}) related to S_0 . The integrated area underneath the $m/e = 31$ TPD peak can be taken as a measure of the total CO coverage. Our best estimate of the saturation coverage of CO on $\text{Si}(100)$ at 85 K is 0.5 monolayer, i.e. one CO molecule per Si–Si dimer. In fitting the coverage versus exposure curve in Fig. 1 (dashed line), a fitting constant $\beta = 6.9 \text{ L}^{-1}$ is obtained.

It is interesting to note that the low temperature shoulder of the TPD peak first appears at the same exposure (~ 0.25 L) at which the “knee” in the exposure dependence curve occurs. (The fitting function is smooth and does not reproduce the “knee”.) A possible explanation for this is that the CO molecules have a definite site preference when adsorbing on $\text{Si}(100)\text{-}2\times 1$ and when most of these sites are filled, the CO may adsorb more weakly on secondary state sites on which the CO has a lower sticking coefficient. However, effects due to coverage-dependent interactions cannot be ruled out.

3.2. EELS

As seen in Fig. 2, when $\text{Si}(100)\text{-}2\times 1$ was dosed with 1 L of CO, two EELS peaks at 53 and 260 meV could clearly be observed. The peak at 260 meV is assigned to the C–O stretching vibration mode and is only slightly red-shifted from the free molecular value of 266 meV [14]. This indicates that the CO is only weakly adsorbed on the $\text{Si}(100)\text{-}2\times 1$ surface and therefore the CO–substrate stretching vibration is expected to have a low energy. The peak at 53 meV is attributed to the CO–Si stretching vibration. It is possible that the state seen in the shoulder of the higher exposure TPD peaks has a stretching vibration mode energy that is close to 260 meV and thus cannot be resolved by EELS, which has a resolution of 15 meV FWHM. The locations of both vibrational losses were found to be independent of coverage.

These results are consistent with the 258 and 51 meV $\text{CO}/\text{Si}(100)\text{-}2\times 1$ EEL peaks reported by Bu

and Lin in Ref. [2]. Through comparisons with studies of EELS done on CO adsorbed on metal surfaces and by performing He I UPS and off-specular EELS of CO/Si(100)-2 $\times$ 1, Bu and Lin conclude that CO is adsorbed on top of the dimers on the Si(100)-2 $\times$ 1 surface and has an end-on and upright position and orientation [2].

3.3. Photo-induced desorption

Fig. 3 shows three typical spectra of the photodesorption signal as a function of irradiation time for $^{13}\text{C}^{18}\text{O}$ adsorbed on Si(100)-2 $\times$ 1 at 85 K. The studies were performed with an incident photon wavelength of 313 nm and a lamp intensity of 1.8 mW/cm²; the spectra shown were taken for low (0.1 L exposure), medium (0.15 L), and high (0.7 L) $^{13}\text{C}^{18}\text{O}$ coverages. For all measurements, the desorption signal immediately jumped to the maximum intensity after the shutter was opened at $t = 0$ s and then decayed with further irradiation. The shutter was left open until $t = 300$ s, by which time most of

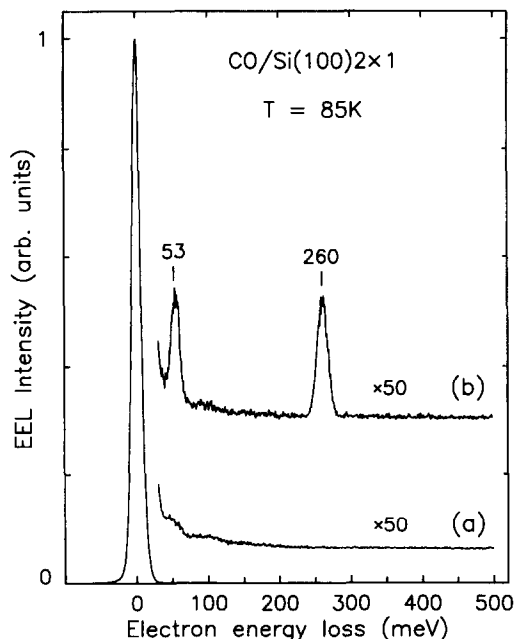


Fig. 2. Electron energy loss spectra of: (a) a clean Si(100)-2 $\times$ 1 surface and (b) Si(100)-2 $\times$ 1 exposed to 1 L CO with the sample temperature at 85 K. The peak at 260 K is taken to be the CO stretch mode and the peak at 53 K is attributed to the Si–CO stretching vibration.

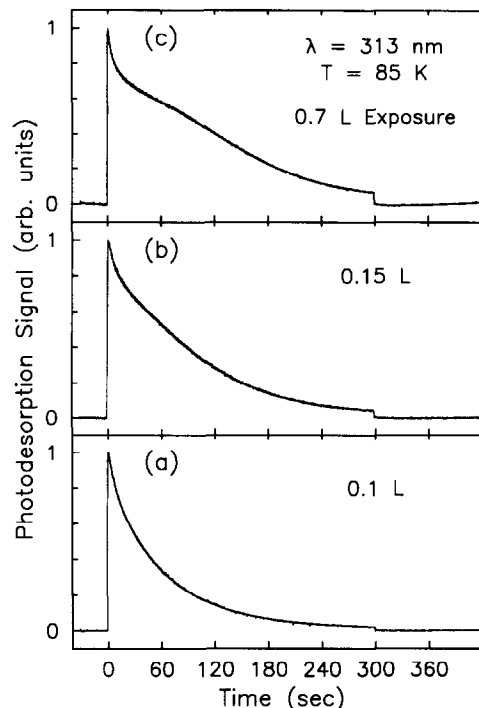


Fig. 3. Three typical photodesorption spectra of $^{13}\text{C}^{18}\text{O}$ from Si(100)-2 $\times$ 1 with initial Si(100)-2 $\times$ 1 exposures of: (a) 0.1 L, (b) 0.15 L and (c) 0.7 L where 1 langmuir (L) = 10^{-6} Torr·s. The sample was initially maintained at a temperature of 85 K and irradiated by photons with a wavelength of 313 nm. The arc lamp shutter was opened at $t = 0$ s and closed at $t = 300$ s. At low $^{13}\text{C}^{18}\text{O}$ exposures, the depletion curve can be described by either one or two cross sections. At higher $^{13}\text{C}^{18}\text{O}$ exposures, the photodesorption signal decays non-exponentially.

the $^{13}\text{C}^{18}\text{O}$ had desorbed. As seen in Fig. 3a, for low coverages and short photon wavelengths (< 400 nm) the photoyield decay curve can be fit very well to a single exponential, $Ce^{-t/\tau}$. For longer wavelengths the photoyield decay is better fit to a sum of two exponentials, $C_1e^{-t/\tau_1} + C_2e^{-t/\tau_2}$, with one of the fitted curves being significantly larger than the other, i.e., the curve is dominated by a single exponential. The presence of two exponentials indicates the existence of two photochemical processes with different cross sections; these may be due to desorption from two different adsorption sites, implying the excitation may be both wavelength-dependent and site-selective. However, the decay is dominated by one species, with contribution from the other species becoming discernible at wavelengths greater than

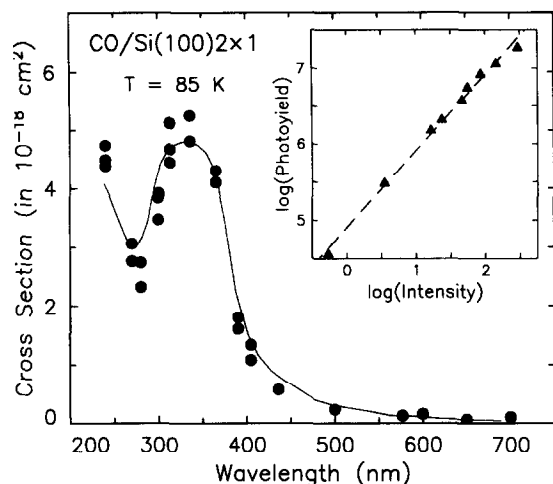


Fig. 4. Wavelength dependence for the photodesorption cross section for a 0.1 L exposure of $^{13}\text{C}^{18}\text{O}$ on Si(100)-2 $\times$ 1 at 85 K. The solid line represents the best fit using the hot-carrier model [6,7,19]. Inset: the dependence of the initial $m/e = 31$ photoyield on the photon beam intensity (313 nm) for a 0.1 L exposure of $^{13}\text{C}^{18}\text{O}$ on Si(100)-2 $\times$ 1 at 85 K.

400 nm. As the initial coverage increases the decay curve becomes more complicated and begins to exhibit non-exponential behavior (Figs. 3b and 3c). The mechanism for this more complicated decay is not understood.

An exposure of 0.1 L was used for the photodesorption wavelength and intensity dependence measurements since the decay curve could be fit to a relatively simple expression: a single exponential curve for wavelengths < 400 nm, and a curve dominated by a single exponential for longer wavelengths. For the intensity dependence measurements, the initial peak in the $m/e = 31$ mass spectrometer signal (at $t = 0$ s) was taken to be a measure of the initial $^{13}\text{C}^{18}\text{O}$ photoyield. The inset of Fig. 4 shows the intensity dependence of the initial photoyield. The plot of $\log(\text{photoyield signal})$ versus $\log(\text{irradiation intensity})$ yields a slope of 1, indicating a linear dependence of the signal on the photon intensity. Therefore, photoyield data taken with different beam intensities can be compared by normalizing to the photon intensity.

The final set of photodesorption studies involved the investigation of the wavelength dependence of the photodesorption. Given the decay constant, τ , the

desorption cross section is calculated for single exponential decays using the relation

$$\sigma = hc/I\lambda\tau, \quad (3)$$

where λ is the incident photon wavelength and I is the irradiation intensity incident on the sample. For the longer wavelength data ($\lambda > 400$ nm), only the cross section calculated from the main decay component was studied for its wavelength dependence since it was clearly the dominant desorption channel. Fig. 4 presents the wavelength dependence of the photodesorption cross section. The cross section increases as the wavelength decreases from the visible to the UV. A rapid increase is observed near 375 nm (3.3 eV) which coincides with the first direct-band-gap transition of Si. The cross section plateaus between 300 and 370 nm and exhibits a dip between 270 and 280 nm. It should also be mentioned that the wavelength dependence of the initial photoyield (the initial peak at $t = 0$ normalized with respect to intensity) exhibits the same behavior.

4. Discussion and conclusions

One area of some concern is the preparation of the Si(100)-2 $\times$ 1 sample. It has been shown that after ion bombardment of a Si(100)-2 $\times$ 1 surface, annealing to 1220 K for 2 min or flashing to 1470 K removes most random or line defects [15,16]. Due to limitations imposed by the sample mounting procedure, the sample used in the study described in this work was annealed to 970 K; therefore, the existence of surface defects is a possibility. However, in the study reported in Ref. [2], the sample was annealed to a temperature of > 1500 K, which should assure a well-ordered surface. The TPD and EELS results described in this work agree well with those reported in Ref. [2], which would not be expected had the CO adsorption occurred mainly on defect sites.

Thermal effects for the observed photodesorption could be ruled out for several reasons. First, a much longer time constant was measured for the surface-temperature rise (≈ 5 s) than the rise time of the photodesorption signal, which was instantaneous within the opening time of the shutter (≈ 0.1 s), and the time profiles of the photodesorption spectra were typically non-thermal [17]. If the desorption was

thermally induced by the light, the mass signal profile would resemble that from TPD since a finite amount of time is required for the temperature to rise [17]. Second, the measured maximum temperature rises during sample irradiation were less than 5 K (sample temperature < 90 K) at the intensities used. Third, had the photodesorption been due to thermal effects, the dependence of the photoyield on lamp intensity, varying over two orders of magnitude, would have been superlinear as opposed to the linear behavior observed.

The dissociation energy for CO in the gas phase is 11.1 eV, and the lowest electronic excitation energies for CO in the gas phase are 6 eV (for a forbidden singlet to triplet transition) and 8.1 eV (for a singlet to singlet transition) [18]. In the present experiments, using 1.8–5.2 eV photons, photodesorption was observed at incident photon energies as low as 1.8 eV (700 nm), with the peak photoyield occurring at photon energies of about 3.7 eV (336 nm). The lowest electronic energy transition of CO could shift to a lower energy upon adsorption; however, it is extremely unlikely that the shift would be as much as 4.2 eV given the very small red-shift in the CO vibrational stretch energy upon adsorption and the low temperature at which CO desorbs from Si(100)-2 × 1. Therefore, it can be concluded that the observed photodesorption is not caused by direct photoexcitation of the adsorbed CO molecule.

A substrate mediated mechanism involving photo-generated hot carriers is the most likely explanation for the observed wavelength dependence of the photodesorption cross section, which can be seen by the following argument [6,7,19]. When the sample is irradiated, electron–hole pairs are created and the total number of electrons or holes created per unit time, per unit surface area is given by $F(1 - R)$, where F is the number of photons incident per unit time, per unit surface area and R is the reflectivity of the substrate. For a simple model, it is assumed that carriers created within a distance δ of the surface have a non-zero, constant probability of inducing adsorbate reactions (desorption), while those created deeper cannot induce desorption. The ratio of the number of photochemically effective photogenerated carriers to the total number of photogenerated carriers is given by $1 - e^{-\alpha\delta}$, where α is the optical absorption of Si. The creation rate of the effective

carriers is therefore proportional to $(1 - R)(1 - e^{-\alpha\delta})$. The desorption cross section correlates with the effective carrier creation rate, therefore the photodesorption cross section can be expressed as [6,19]

$$\sigma = g [F(1 - R)(1 - e^{-\alpha\delta})]^m, \quad (4)$$

where m is the power dependence of the photoyield on the incident radiation intensity ($m = 1$ for a linear dependence). It is expected that the parameters g and δ vary with the carrier energy and momentum, and therefore photon wavelength.

The wavelength dependences of $(1 - R)$ and α for Si at the correct incident angle were calculated from published optical parameters [20]. The absorption coefficient exhibited large changes over the wavelength region of interest, especially near 375 nm due to the onset of the first Si direct-bandgap transition. The dip between 270 and 280 nm arises from the combined wavelength dependences of R and α [6]. For simplicity, the parameters g and δ were taken to be constants for the fit. The best fit to Eq. (4) is shown as the solid line in Fig. 4, resulting in an interaction distance of $\delta = 25 \pm 5$ nm, which is on the order of the mean free path for the carriers. A similar wavelength dependence of the photoyield (which correlates with the desorption cross section) was observed for NO/Si(111)-7 × 7 and application of the model described above resulted in a value of $\delta = 20 \pm 3$ nm for the effective carrier depth [6].

When hot carriers (electrons and holes) are produced under photon irradiation, the electronic structure at the surface of the substrate is perturbed. This perturbation may cause an excitation in the electronic state of the adsorbate–substrate system, making CO bonding to the surface unfavorable. To further understand the nature of the electronic excited states (e.g., whether it involves transient positive or negative CO ion states), the energy levels of the adsorbate need to be examined. Rough estimates of the positions of the highest occupied (the 5σ level, the 1π level, or an overlap of the two) and lowest unoccupied (2π) molecular levels of CO adsorbed on Si(100)-2 × 1 were made by plotting the energy level positions of CO adsorbed on transition metal surfaces: Ag, Ni(100), Ni(110), Ni(111), Cu(100), Cu(110), Cu(111), Pt(110), Pt(111), Pd(100) and Pd(111) as a function of desorption temperature [21–

24]. The desorption temperature, for comparable heating rates, was used as an indication of adsorbate–substrate interaction strength; the stronger the interaction, the further the CO energy level values should be from their gas phase values: -14 and $+1.5$ eV with respect to the vacuum for the 5σ and 2π levels, respectively. The 2π and 5σ levels of CO/Si(100)- 2×1 were then estimated by determining a best straight-line fit to the combined CO/metal data and evaluating the energy at the CO/Si(100)- 2×1 desorption temperature of 171 K.

Two sets of comparison plots were made, one set made from data referenced from the vacuum level, and one set from data referenced from the substrate Fermi level. The plots referenced from the vacuum level (vacuum = 0 eV) produced estimates of -0.4 ± 1 eV and -13.1 ± 1 eV for the 2π and 5σ levels, respectively, of CO when adsorbed on Si(100)- 2×1 . The plots made using data referenced from the substrate Fermi level ($E_F = 0$ eV) produced an estimate of 4 ± 1 eV for the 2π level and -8.7 ± 1 eV for the 5σ level. In determining the energy of the 2π level, the plot referenced from the vacuum level showed a clearer correlation between the energy position of the level and the desorption temperature. For the 5σ level, the plot referenced from the Fermi level showed a better correlation with less scatter. However, both estimates resulted in an energy difference of 12.7 eV between the highest occupied and lowest unoccupied levels of CO/Si(100)- 2×1 . These estimates indicate a work function of about 4.4 eV for Si(100)- 2×1 with adsorbed CO, which is reasonable considering the 4.87 eV for a clean surface [25].

The He I UPS valence band spectra of CO/Si(100)- 2×1 taken by Bu and Lin [2] indicate that no change in the band bending is caused by the adsorption of CO. There is no reason the band gap of Si(100)- 2×1 should be affected by CO, so we can assume that the positions of the conduction band minimum and valence band maximum of Si(100)- 2×1 in relation to the Fermi level should not change from their clean Si(100)- 2×1 values upon CO adsorption. The valence band maximum of Si(100)- 2×1 is located 0.46 eV below the Fermi level and Si(100)- 2×1 has an indirect bandgap of 1.11 eV [26]. An energy level diagram of the CO/Si(100)- 2×1 system, using our estimates of the CO molecular

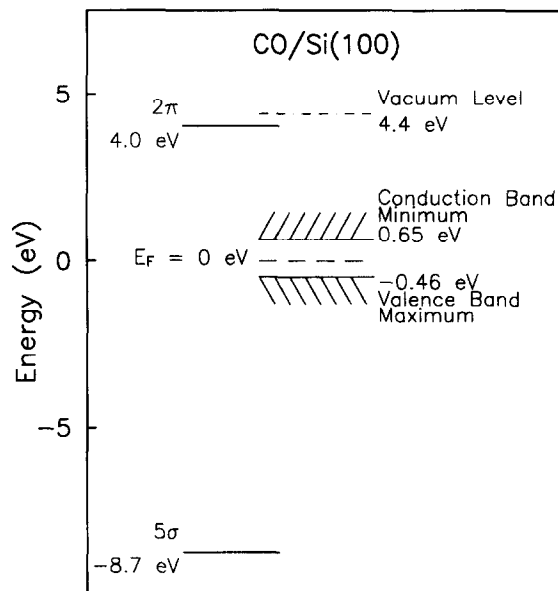


Fig. 5. Schematic energy level diagram of the CO/Si(100)- 2×1 system. The positions of the 2π and 5σ levels were estimated by comparisons with CO/transition metal data.

level positions, is shown in Fig. 5. It is improbable that a photoexcited hole can tunnel from the substrate into the highest occupied adsorbed CO state due to the large energy separation between the conduction band minimum and the highest occupied CO level (~ 9.4 eV). If there is any transient charge transfer between the substrate and adsorbate, it is most likely from photoexcited substrate electrons to the CO 2π level, since the energy between the lowest unoccupied CO state and the valence band maximum is ~ 4.5 eV (photon wavelength of ~ 280 nm).

The fit of the model described in this paper to the data in Fig. 4 indicates that the behavior of the photodesorption wavelength dependence curve is dominated by the optical properties of the Si substrate. The position and width of the CO resonance levels (occupied or unoccupied) are not reflected in the wavelength dependence of the photoyield. It is clear that substrate electronic excitations provide the driving force for the photodesorption of CO. Our picture of bonding, as depicted in Fig. 5, is an approximation. The position of the 5σ level is de-

duced from photoemission data, which reflects the creation and relaxation of a positive ion state. Similarly, a negative ion state is involved in inverse photoemission, which is used to deduce the position of the 2π level. For wavelengths longer than 280 nm, the CO/Si(100)- 2×1 system as a whole remains neutral; no electrons are ejected (or introduced). It is therefore necessary to consider the interactions of CO with Si more rigorously and to obtain an accurate description of the bonding and antibonding states of the CO/Si(100)- 2×1 system. Eventually, within subpicosecond time scales, electronic excitations force the nuclei in the system to respond to the changes created in the energetic and spatial distributions of the electrons; the nuclei need to seek a new low energy state corresponding to the newly created electron configuration. The nuclei will suddenly find themselves in the “wrong” positions. The excited electronic configuration results in forces on the nuclei, and it is the subsequent adjustment of the nuclei which leads to photodesorption. This whole process, however, is a dynamical one and a rigorous treatment is necessarily complicated for an extended system. Nevertheless, the wavelength dependence data and the fit to Eq. (4) in Fig. 4 suggest that the magnitude of the photoyield depends on the number of carriers created within a short distance (on the order of δ) of the adsorbed molecules. The excited carriers may lose their influence on the adsorbed molecules if they scatter, which may prevent them from propagating the initial disturbance created by photoabsorption at depths exceeding this distance to the molecules on the surface.

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