

Study of clean and CO-covered Ge(111) surfaces by photoemission and ion-neutralization spectroscopies

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Chemisorption of carbon monoxide (CO) on the Ge(111) 2×8 surface was investigated using ultraviolet photoemission spectroscopy (UPS) and ion-neutralization spectroscopy (INS). It was found that CO molecules are not adsorbed on the Ge(111) surface unless they are activated. Once activated by hot tungsten filaments, CO molecules are chemisorbed nondissociatively at room temperature with a small sticking coefficient (~ 0.001). Both UPS and INS show that CO saturates the (111) surface to produce four CO-associated features at $E - E_{\text{VAC}} = -7.0, -9.5, -12.0,$ and -14.2 eV in the surface electronic density of states. The feature at highest energy is identified as an enhanced Ge p -like valence band due to CO molecules on the surface. The remaining three peaks at $-9.5, -12.0,$ and -14.2 eV are related to the $5\sigma, 1\pi,$ and 4σ orbitals of the free CO molecule, respectively. These spectral features are significantly different from those for CO adsorption on a number of transition metals. Simultaneous use of INS and UPS provides us with complementary information on the present chemisorption system, on the basis of which we propose that the CO molecule occupies upon adsorption the threefold interstitial site with the carbon atom toward the bulk and the oxygen atom toward the vacuum.

I. INTRODUCTION AND SUMMARY

The adsorption of simple gases on Si or Ge has been the subject of a number of recent studies.¹⁻⁷ The reconstructive chemisorption of atomic hydrogen on various Si or Ge surfaces has provided us with information that may lead to a better understanding of the geometrical reconstruction of the starting clean surface.⁶ Studies of oxygen adsorption revealed that the reaction of oxygen with Si surfaces involves two distinctively different processes, first, chemisorption of gas molecules and second, oxidation to form SiO_2 layers.^{2,3}

Here we report the study of CO adsorption on the Ge(111) 2×8 surface by ion-neutralization spectroscopy (INS), ultraviolet photoemission spectroscopy (UPS), Auger-electron spectroscopy (AES), and low-energy electron diffraction (LEED). There has been no detailed study of this system to date. CO adsorption on some transition metals (Ni, Pt, Rh, and Pd) has been studied recently by a number of groups.⁸⁻¹⁰ These studies have concluded that CO adsorbs nondissociatively on a metal surface such that the molecular axis is perpendicular to the surface with the carbon atom closest to the metal. In these cases the bonding results mainly from interaction between the nonbonding molecular 5σ electrons of

CO and the metal d electrons, as is evident from the large downward shift in energy of the 5σ orbital and its mixing with the 1π orbital upon adsorption.

Our findings indicate that CO adsorption on the Ge(111) surface differs in several ways from CO adsorption on metals. First of all, CO molecules are not adsorbed on the Ge(111) surface unless they are activated. When CO is thermally activated, adsorption takes place at a very slow rate. Second, the observed surface electronic structure of CO on Ge(111) is found to be markedly different from that of CO on a metal surface. We identify four CO-associated peaks at $E - E_{\text{VAC}} = -7.0, -9.5, -12.0,$ and -14.2 eV in the surface density of states instead of two resonance peaks as observed for CO on some metals. The simultaneous use of two electron spectroscopies, UPS and INS, helps us to identify the orbital nature of these resonance states.^{11,12} In the order of increasing bonding energy these resonances are an enhanced Ge p -like valence band in the near-surface bulk, and the $5\sigma, 1\pi,$ and 4σ orbitals of the adsorbed CO molecule. Although the available data do not give a clear answer to questions as to the nature of the CO activation and the structure of the adsorbed carbon monoxide, we propose a type of activation and a possible adsorption site that resembles that of chlorine on Ge(111).^{13,14} Similar results were obtained for CO adsorption on Si.¹⁵

II. EXPERIMENTAL TECHNIQUES

The vacuum system used in this study has been described elsewhere.¹⁶ It provides at different ports three electron spectrometers for INS, UPS, AES, and a LEED system. Surface preparation by sputtering the semiconductor sample in a glow discharge is carried out at the fourth port that is shielded from the other ports. The base pressure was $\sim 5 \times 10^{-11}$ Torr with the working pressure $\sim 1 \times 10^{-10}$ Torr. A 2π solid angle, high-pass, hemispherical grid analyzer with an energy resolution of approximately 0.4 eV was used for all the measurements of electron energy distributions. Although this type of energy analyzer may not be suitable for the study of final-state symmetry¹⁷ and polarization effects in angle-resolved photoemission, it has the advantage that diffraction effects are minimized in the measured, angle-integrated, electron energy distributions. The light source for photoemission was a differentially pumped glow-discharge lamp operated with He, Ne, and Ar in the pressure range 0.1 to 5 Torr with the pressure in the main chamber below 10^{-7} Torr. In this paper all energies in the UPS spectra will be referred to the vacuum level E_{VAC} . The point $E - E_{\text{VAC}} = -\hbar\omega$ at which kinetic energy is zero was determined in each spectrum by a linear extrapolation of the low-energy secondary peak. The error introduced by this procedure is estimated to be not more than ± 0.2 eV.

In INS monoenergetic 10-eV He^+ ions were focused on the target surface with normal incidence and the kinetic energy of Auger ejected electrons was obtained with an energy resolution of ~ 0.4 eV. Sequential deconvolution of the fold function derived from the Auger-electron energy distribution yields the unfold function, $U(E)$, whose origin is at the top of the valence band (E_V).¹⁸ $U(E)$ is closely related to the local electronic density of states in the region between the surface and the position of the ion at neutralization. The placement of the unfold function with respect to the vacuum level is uncertain to perhaps ± 0.5 eV using INS parameters only. This results principally from our lack of knowledge of the precise value of the effective neutralization energy, E_n' , of the He^+ ion near the solid surface and some uncertainty in determining the maximum electron kinetic energy. In this study $U(E)$ is placed relative to the UPS spectrum so that the main resonance peaks in the two spectra coincide.

The Ge target was cut from a 0.25-mm-thick wafer into a 7×14 -mm rectangular shape and mounted via tantalum clamps on the target manipulator. The target manipulator is a two-axis target-positioning mechanism with which it is possible to move the target from port to port in the apparatus as well as to vary the angle of incidence of the photon or ion beam from -15° to 70° .¹⁹

The Ge(111) face was sputtered for 30 minutes

with 150-eV Ne^+ ions produced in a glow discharge in Ne at a pressure of approximately 10^{-2} Torr. This removed approximately 1000 monolayers. The target was held at 400°C for the first five minutes of sputtering and at room temperature thereafter. Annealing of the target after sputtering for five minutes at 500°C drove out all the Ne gas trapped inside and produced a sharp 1×1 LEED pattern with some fuzzy spots around the nonintegral 2×1 spots. It was necessary to anneal the target at 650°C for 10 minutes in order to obtain a sharp, three-domain, 2×8 LEED pattern. It may be worthwhile mentioning that Ne^+ ions used as sputtering agents have a clear advantage over Ar^+ ions. While the rates of sputtering with Ne^+ and Ar^+ ions at the Ge(111) surface are comparable, the damage caused by Ne^+ ions is considerably less than that by Ar^+ ions. The regrowth rate of Ge is approximately $30 \text{ \AA}/\text{min}$. at 550°C after Ne^+ ion sputtering, more than 10 times faster than that after Ar^+ ion sputtering ($\sim 2 \text{ \AA}/\text{min}$).²⁰ Thus the minimum annealing temperature is lower and the annealing time is shorter using Ne^+ ions rather than Ar^+ ions. Furthermore, the pumping speed for Ne gas is faster than that of Ar, and Ne does not condense on the wall of the liquid-nitrogen trap.

INS and UPS data were taken on the surface having a good quality 2×8 LEED pattern to check its chemical purity. A series of annealings at 650°C were carried out until we obtained stable and reproducible terminal INS and UPS spectra. We also required that all AES signals of impurities be below the noise level. Peak-to-peak noise in the differential Auger spectrum is approximately 100 times smaller than the peak-to-peak signal of the Ge feature at 1140 eV.

After a clean surface had been produced, contaminants on the surface from the residual gas could be removed without difficulty by heating to 600°C for 10 sec. During CO exposures the partial pressure of CO ranged from 2×10^{-7} to 7×10^{-6} Torr and the pressure of other gases, mainly CO_2 and a small amount of O_2 , increased slightly but never exceeded more than 0.1% of the CO gas pressure. It is unlikely that the surface was contaminated by impurity gas during CO exposure since CO_2 does not interact with the Ge(111) surface at room temperature. It was found that the CO-covered Ge(111) surface was fairly inert to contamination as had been found for the hydrogen-covered Ge(111) surface.^{6,21} All CO exposures were performed with the Ge(111) surface at room temperature.

III. EXPERIMENTAL RESULTS

A. Clean Ge(111) surfaces

As indicated above, we observed during the preparation of the clean (111) 2×8 surface an inter-

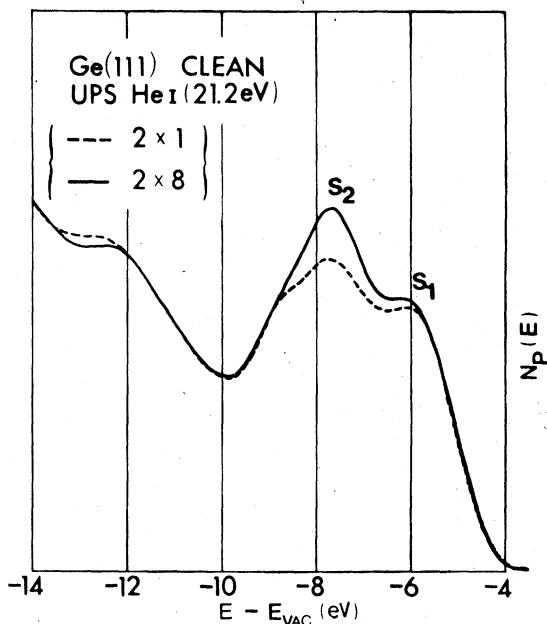


FIG. 1. He I ($\hbar\omega = 21.2$ eV) UPS spectra for the annealed Ge(111) 2×1 surface and the annealed Ge(111) 2×8 surface.

mediate surface phase that is characterized by fuzzy 2×1 spots superposed on the 1×1 LEED pattern. AES showed no impurity on this surface suggesting that this is also a clean surface. A He I ($\hbar\omega = 21.2$ eV) UPS spectrum for this 2×1 surface is given in Fig. 1. This surface was stable and was reproduced repeatedly. The Ge(111) 2×8 surface was obtained by heating the 2×1 surface at 650°C for 10 minutes or more.

The clean Ge(111) surface with a 2×8 LEED pattern yielded the other UPS spectrum shown in Fig. 1. Differences in the UPS spectra for the 2×8 and 2×1 surfaces are limited to the two regions near $E - E_{\text{VAC}} = -7$ and -13 eV. The spectrum for the 2×8 surface has two peaks in the p band, the major peak at $E - E_{\text{VAC}} = -7.7$ eV, and a shoulder at -6 eV, while that for the 2×1 surface has an additional shoulder at -9 eV making it appear similar to a Si(111) 7×7 spectrum. Following Rowe's assignment in the case of the cleaved Ge(111) 2×1 surfaces,²¹ we assign the peaks at -6 eV and the -7.7 eV to intrinsic surface states of the dangling-orbital type (S_1) and the back-bond type (S_2), respectively.

Figure 2 shows INS electron energy distributions, $N_I(E)$, for 10-eV He^+ ions on both clean and CO-covered Ge(111) 2×8 surfaces. Curve 1 for the clean 2×8 surface is essentially identical to that obtained in earlier work reported by Hagstrum and Becker.²² The unfold function [curve 1 of Fig. 3(b)], obtained from these data by sequential deconvolution using $E_n' = 22.5$ eV shows two peaks S_1 and S_2 , at

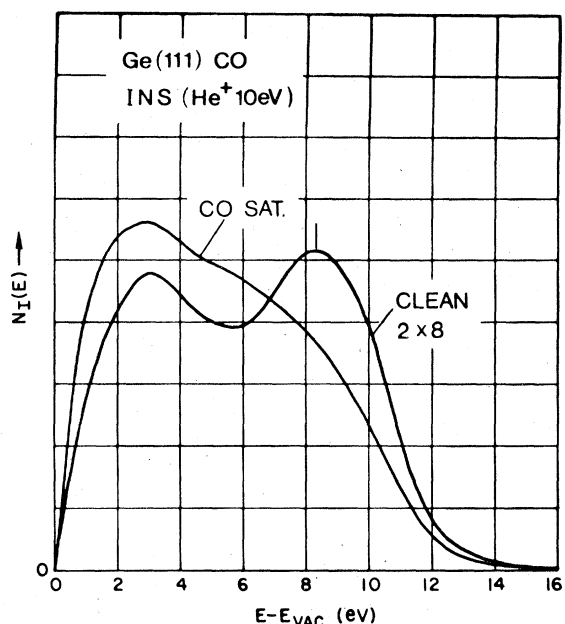


FIG. 2. Kinetic energy distributions (closely related to the fold functions) of Auger electrons ejected from the clean and CO-saturated Ge(111) surfaces by the neutralization of 10-eV He^+ ions.

$E - E_{\text{VAC}} = -5.8$ and -7.6 eV, respectively, in the p -like valence band as does the UPS spectrum for the clean surface, curve 1 of Fig. 3(a).

It is seen that the first peak S_1 in $U(E)$ is considerably more intense than the second peak S_2 . This is understandable since the first peak S_1 is supposed to result from the dangling-orbital surface resonance whose wave function sticks out into the vacuum perpendicular to the surface Ge layers. As a result, this resonance can interact strongly with the incoming He^+ ions. The second peak is due to the back-bond-type surface resonance which interacts less strongly with the He^+ ions.¹¹ The relative intensity of the S_1 and S_2 peaks in the UPS spectrum [curve 1 of Fig. 3(a)] is certainly affected first by the fact that both types of surface resonance lie well within the sensitivity volume of UPS and second by the relative UPS transition probabilities which can differ appreciably from those of INS. At 21.2 eV UPS sensitivity to surface states S_1 and S_2 has been shown by Pandey and Phillips to be considerably smaller than the sensitivity to the p -like valence band.²³ We note that the broad feature in curve 1 of Fig. 3(b), centered at -12 eV in the s portion of the valence band, has considerably greater relative intensity than does the corresponding feature in $N_p(E)$, curve 1 of Fig. 3(a), as a result of greater relative INS sensitivity to s -like wave functions.

We now make some observations concerning the 2×8 LEED pattern of the clean Ge(111) surface and

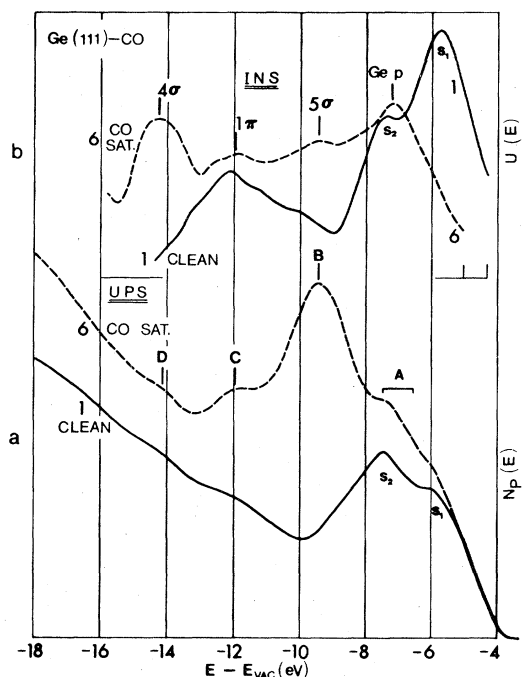


FIG. 3. Graph showing UPS spectra ($\hbar\omega = 21.2$ eV) at (a) and the unfold functions $U(E)$ from INS at (b), in each case for the clean and CO-covered Ge(111) surfaces. The INS spectra are derived from the data shown in Fig. 2 and their origins are indicated by the scale marks at the right-hand side. Note that the $U(E)$ curves have been placed relative to the $N_p(E)$ curves so that the S_1 and S_2 peaks appear at the same energies in the two spectra.

the sensitivity of the structure to heating and exposure to atomic hydrogen. In the first place the so-called 2×8 pattern for the clean surface does not show all possible 2×8 nonintegral superstructure spots. In this respect it differs markedly from the Si(111) 7×7 pattern, for example. The Ge(111) 2×8 pattern consists of the integral spots (0,0), (0,1), and (1,0) and only the following nonintegral superstructure spots: $(\frac{4}{8}, 0)$, $(\frac{1}{8}, \frac{1}{2})$, $(\frac{3}{8}, \frac{1}{2})$, $(\frac{4}{8}, \frac{1}{2})$, $(\frac{5}{8}, \frac{1}{2})$, and $(\frac{7}{8}, \frac{1}{2})$. All of these superstructure spots disappear when the surface is heated to 250 °C or is exposed to atomic hydrogen. These observations are contrary to the findings on other surfaces, such as Si(111) 7×7 and Ge(100) 2×1 ,²⁴ where many of the features of the original LEED patterns persisted throughout heat treatment or exposure to atomic hydrogen. All of these observations imply that the 2×8 surface reconstruction is not particularly stable, having a surface Debye temperature much lower than that for Si(111) 7×7 . Although it is difficult to reach a clear and definitive conclusion as to the nature of the 2×8 surface reconstruction, the above findings do not favor the vacancy model suggested by Lander.²⁵ Since the vacancy formation energy for Ge

of 2.4 eV is rather large and even higher than that for Si,²⁶ vacancies on Ge(111) are unlikely to disappear by low-temperature heating or H adsorption.

B. CO adsorption on the Ge(111) 2×8 surface

The clean Ge(111) 2×8 surface was exposed to CO gas at a partial pressure of 7×10^{-6} Torr. We found that CO molecules do not adsorb on this surface if all the filaments in the vacuum station are turned off.²⁷ Under these conditions we see no change at all in the He I UPS spectrum with CO exposure up to 10^4 L (1 Langmuir = 10^{-6} Torr sec). LEED and AES taken at the end of the exposure also corroborate this UPS result showing no changes from the clean surface.

It is known that the presence of a hot filament in the vacuum system can sometimes appreciably affect the results of chemisorption experiments.²⁷⁻²⁹ Contact with a heated surface or excitation by thermionic electrons can activate or even dissociate a molecule. We have tried CO exposures at a CO partial pressure of 1×10^{-6} Torr with the tungsten filaments inside our sputtering device held at 1500 °C. Under these

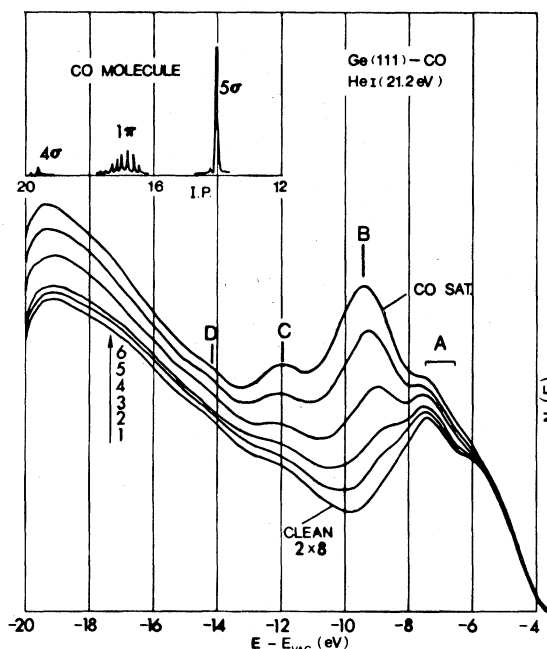


FIG. 4. Family of He I UPS spectra (curves 1 through 6) for the Ge(111) 2×8 surface during its exposure to activated CO molecules. The CO pressure was 6×10^{-6} Torr and the tungsten filaments were held at 1500 °C. The exposure times in minutes are: curve 1: 0 (clean); curve 2: 5; curve 3: 10; curve 4: 20; curve 5: 40; and curve 6: 80 (CO saturated). The molecular photoelectron spectrum of carbon monoxide, plotted against ionization potential (I. P.), is shown in the inset at the upper left [Ref. 31].

conditions both UPS and INS showed that the electronic structure of the surface was changing from that of the clean surface. Figure 4 shows a family of the He I UPS spectra obtained during this type of CO exposure. At the beginning CO adsorption is slow, indicating an initial sticking coefficient of less than 0.001. We could see four peaks or features, *A*, *B*, *C*, and *D*, developing at $E - E_{VAC} = -7.5$, -9.5 , -12 , and -14 eV, respectively, as CO exposure increased. After 90 minutes of CO exposure we reached the terminal UPS spectrum, curve 6 of Fig. 4, and have assumed it to be the UPS spectrum for the CO-saturated Ge(111) surface.

UPS spectra for the clean and CO-covered surfaces were also obtained using Ne I (16.8 eV) and Ar I (11.7 eV) radiation and these are compared with the corresponding He I UPS spectra in Fig. 5. The Ne I and He I UPS spectra are quite similar as to peak po-

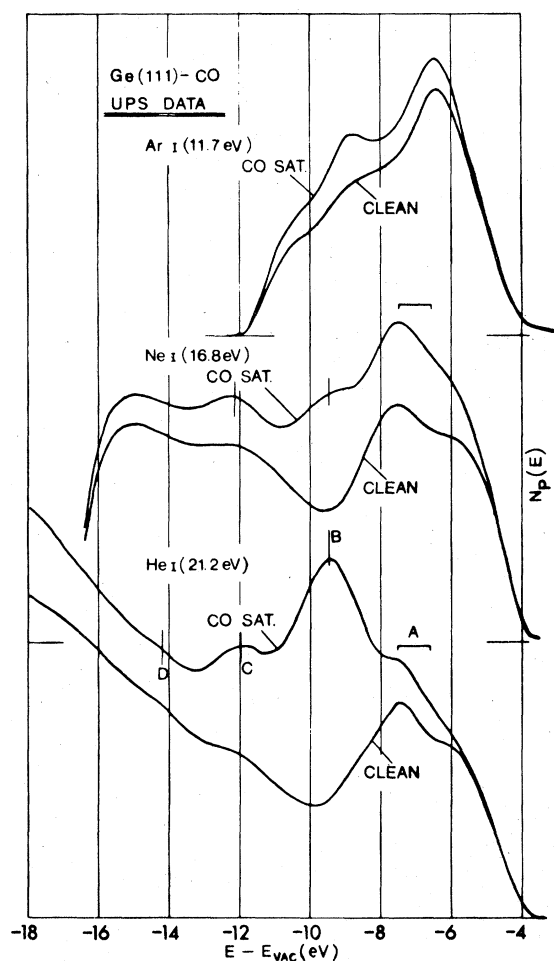


FIG. 5. UPS spectra for the clean and CO-covered Ge(111) surfaces obtained using three different uv photon energies. In the case of Ar I radiation, the spectra are dominated by the joint density of states.

sitions and heights suggesting that the UPS spectra at these photon energies essentially present the features of the one-electron state density of occupied states, that is, the density of initial states in the UPS sensitivity volume modified by transition matrix element effects.³⁰ In the case of Ar I radiation the UPS spectra for the CO-saturated and clean surfaces are very different from those obtained using Ne I and He I radiation indicating a dependence at this photon energy on the joint density of initial and final states. We shall proceed with our argument concerning the nature CO adsorption on the (111) surface on the basis of the He I (21.2 eV) UPS spectra.

Throughout the CO adsorption, the UPS data showed that the position of the Fermi level at the Ge(111) surface ($E_{VAC} - E_F$) changed by less than 0.02 eV. The highest kinetic energy of the photoemitted electrons remained the same before and after the CO adsorption. Thus CO adsorption brings about no diminution in UPS spectral intensity at the energy position of the dangling-orbital surface states. However, there is little doubt as to the existence of the surface states at $E - E_{VAC} \sim -6$ eV for the clean 2×8 surface.³⁰ When a clean 2×8 Ge(111) surface is exposed to atomic hydrogen, or to molecular oxygen,²³ the peak at $E - E_{VAC} \cong -6$ eV disappears completely. [This also occurs for the clean Si(111) 7×7 surface]. It is possible that the disappearance of the surface states on CO adsorption is masked by an increase of the overall *p*-like valence band in the same energy region, but our UPS data alone do not demonstrate this. In the INS unfold function of Fig. 3(b) we see that the surface state peak S_1 , which is strongly observed in $U(E)$ for the clean surface, has almost completely disappeared in $U(E)$ for the CO-saturated surface. We are thus led to believe that the dangling-orbital surface states do disappear upon CO adsorption but that this change is masked in the UPS spectrum, curve 6 of Fig. 3(a), by an increase in the Ge local density of states in the energy range of the *p*-like valence band. Except for this difference in the energy region around $E - E_{VAC} = 5.8$ eV, the INS and UPS spectra [curves 6 of Fig. 3(a) and (b)] are similar, each having four resonances *A*, *B*, *C*, and *D*, due to CO adsorption, although the intensities of these peaks are interestingly different in the two spectra. This difference in observed intensity between the two electron spectroscopies can also help us to identify the bonding nature of the orbitals involved. Here, $E_n' = 23.2$ eV was used to place the INS unfold function, curve 6, in accord with the UPS spectrum for the CO-covered surfaces.

It is of interest to consider the difficult question of the nature of the activation of CO at the hot W filaments. Although CO is known to be dissociated when *on* metal surfaces it is also known that it is nevertheless desorbed as the molecule. We calculate the probability of desorption of dissociated CO into

the gas phase as about 10^{-6} at a CO partial pressure of 10^{-6} Torr. Although we cannot make a similar calculation for excitation of the molecule to the $3^1\Pi$ state we remark that the Boltzmann factor for population of this state 6 eV above the $1^1\Sigma$ ground state is very small. We believe the most probable excitation is vibrational. At 1500°C approximately 15% of the CO molecules are excited into the first vibrational level 0.25 eV above the ground state. We have found that the position of the hot filaments with respect to the Ge sample face had no significant effect and that direct view of the sample face from the hot filaments was not necessary to produce CO adsorption.

Regardless of the nature of the CO activation, it is quite clear that CO molecules are adsorbed on the Ge(111) surface at room temperature without dissociation. In Fig. 6 we have compared the UPS spectra for the clean Ge(111) surface and for this surface modified by adsorption or oxidation. The three modified surfaces are the Ge(111) surface with adsorbed CO (curve 2), with adsorbed O_2 (curve 3), and when oxidized (curve 4). Molecular oxygen produced the structure seen in curve 3 of Fig. 6, namely, a main peak at $E - E_{\text{VAC}} = -10$ eV with two small shoulders at -8 and -12 eV, and a weak peak at -14.5 eV. This spectrum has structure essentially

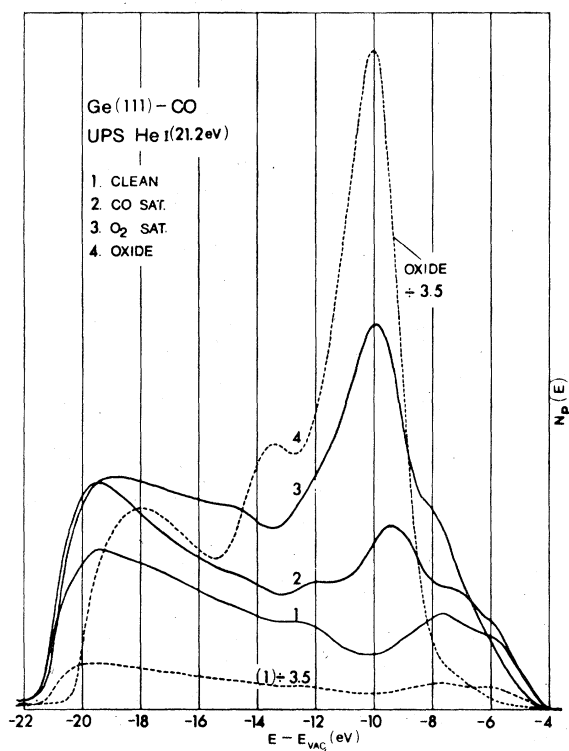


FIG. 6. He I UPS spectra for 1, the clean; 2, the CO-saturated; 3, the O_2 -saturated; and 4, the oxidized Ge(111) surface, curves 1–4, respectively.

similar to that of the photoemission spectrum of a silicon surface covered with a monolayer of oxygen molecules,³ though the peak positions differ. The decrease of emission intensity in curve 3 in the range $-4 > E - E_{\text{VAC}} > -6$ eV relative to curve 1 is due mainly to the disappearance of the dangling-orbital surface states upon O_2 adsorption. The AES spectra taken simultaneously show that the amount of oxygen on the O_2 -saturated Ge(111) surface (curve 3) is almost four times that for the CO-saturated surface (curve 2).

In the case of the oxide layer on Ge we did not obtain within a reasonable exposure time a terminal UPS spectrum which we could assign to the saturated surface. However, the structure of the UPS spectrum does not change above 300-L oxygen exposure. Thus we have plotted the He I UPS spectrum for 300-L oxygen exposure, curve 4 of Fig. 6, as the oxidized surface. Curve 4 has been placed on the $E - E_{\text{VAC}}$ scale so as to have a common Fermi level with curve 3. The required shift is visible as the separation of the deep band edges of curves 3 and 4.

Another interesting observation of a qualitative difference among the surfaces compared here is that the oxygen peak at about 500 eV in the AES spectrum for the CO-saturated surface is different from those observed for oxygen adsorption on Ge(111) not only in intensity but also in structure. The oxygen peak for the CO-covered surface has an additional peak near 540 eV on the higher-energy side not seen in other cases. This suggests that the bonding of oxygen in the CO-saturated Ge(111) surface is different from that in the surface with adsorbed oxygen only. Based on the above experimental results, it is clear that the characteristics of the CO-saturated surface are different from those of the surfaces with oxygen only, carbon only, or with a linear combination of these two elements. Thus we conclude that CO molecules are adsorbed on the Ge(111) surface non-dissociatively at room temperature. Based on this conclusion we shall attempt to interpret the INS and UPS data.

IV. INTERPRETATION OF THE EXPERIMENTAL DATA

According to our INS results, feature *A* at $E - E_{\text{VAC}} \sim -7.0$ eV in the UPS spectrum of Fig. 3(a) is not really a new structure associated with adsorbed CO but is rather an enhancement of photoemission intensity of the Ge *p*-like valence band due to the presence of the adsorbate. The three other peaks, *B*, *C*, and *D*, are most probably associated with the 5σ , 1π , and 4σ molecular orbitals of CO, respectively. Ionization potentials of the 5σ , 1π , and 4σ states in the gas phase are 14.0, 16.9 and 19.7 eV, respectively.³¹ (See inset in Fig. 4.) Whereas these three numbers have pairwise separations of 2.9 and

2.8 eV, the energy positions *A*, *B*, *C* have separations of 2.5 and 2.4 eV, respectively. Furthermore, the relative intensities of peaks *B*, *C*, and *D* in the UPS spectrum, curve 6, agree reasonably well with those of the 5σ , 1π , and 4σ levels of the gas phase CO molecule. Assignment of peaks *B*, *C*, *D* to the 5σ , 1π , and 4σ orbitals of adsorbed CO requires energy shifts of 4.5, 4.9, and 5.4 eV, respectively. These are all rather large compared to the usual values of 2 to 3 eV reported for many chemisorption systems. However, large energy shifts have been reported in some chemisorption systems, such as Ge(111):H or Si(111):H, where $1s$ states of H shift approximately 4 eV.^{6,24} The uniform shifts of peaks *B*, *C*, and *D* can be understood if we assume that both carbon and oxygen atoms interact with the Ge substrate to some degree while maintaining the molecular features of CO.

As we have pointed out previously the three-peak structure (*B*, *C*, and *D*) observed here is uniquely different from the two-peak structure of CO adsorbed on a number of transition metals.⁸⁻¹⁰ In those cases, CO molecules are adsorbed on the metal surfaces at room temperature without being activated and in all cases the carbon atom interacts almost exclusively with d -band electrons of the metal via the 5σ orbital of the CO molecule, causing the 5σ level to be pulled down and mixed with the 1π orbital. In the present system the 5σ orbital is shifted from the position in the free molecule less than the 1π and 4σ , but not enough less to have it mix with the 1π orbital. Furthermore, there is little possibility that CO adsorption on Ge(111) resembles physisorption. Relaxation energy shifts for physisorption are in the range 1 to 1.6 eV and cannot be as large as those indicated here.³² Thus the required activation of the CO molecule and the fact that temperatures in excess of 250 °C are required to desorb it appears to preclude physisorption.

Based on these experimental results we suggest that the CO adsorption on the Ge(111) surface represents a chemisorption system in which the oxygen atom as well as the carbon atom participates in the bonding with the substrate Ge.

V. ADSORPTION GEOMETRY OF CO ON Ge(111)

Since no theoretical study of the system CO on Ge(111) has been reported to date, it is not easy to specify the adsorption geometry or the adsorption site. However, the experimental results we have presented here do suggest a plausible model for the nondissociative CO adsorption on the Ge(111) surface. Comparing the INS spectrum, curve 6 of Fig. 3(b), with the corresponding UPS spectrum, curve 6 of Fig. 3 (a), one realizes that INS strongly detects the 4σ orbital, containing principally oxygen p electrons, while the 5σ orbital, containing mainly carbon

p electrons is observed very weakly. We take this as convincing evidence that the oxygen atom lies closer to the surface than does the carbon atom. Were the carbon atom outermost, its 5σ orbital, which has the greatest intensity among the three orbitals in the electron spectrum of free CO, should certainly produce the main resonance peak in the INS unfold function contrary to our observation.

As to the adsorption site, we consider only two possibilities because of the high symmetry of the (111) 1×1 surface: atop the surface Ge atom (the covalent site) or in an open site at the center of the surface triangle (the interstitial site).¹³ If the CO molecule occupies the covalent site, the interaction between it and the Ge surface takes place mainly via its 5σ orbital. In this case we would expect a relatively smaller shift of the energy of the 5σ orbital from the free-space orbital energy than is observed in this experiment. It is true that this shift for the 5σ is 4.5 eV which is smaller than the 4.9 and 5.4 eV shifts for the 1π and 4σ , respectively. As noted earlier, however, the 5σ and 1π mix for "covalent" adsorption of CO on a transition metal. If the CO molecule were to recede into the space between the first and second layers of the Ge(111) surface at the interstitial site (Fig. 7), it is natural to expect that all three orbitals, 5σ , 1π , and 4σ would participate in the interaction with the substrate with smaller variations among the orbital shifts from the orbital energies of the free molecule. The CO molecule is small enough

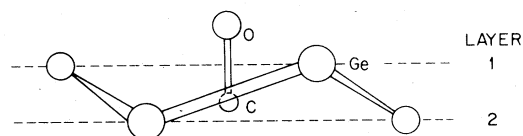
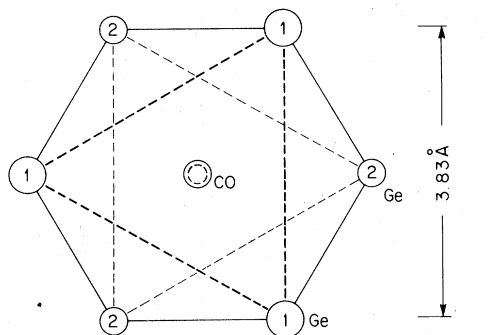


FIG. 7. Schematic views of the proposed model for the CO adsorption site at the center of the void formed by Ge atoms in the first and second layers. First and second layer Ge atoms are labeled 1 and 2, respectively. A top view (upper part of figure) and a side view (below) are shown.

in size to occupy this interstitial site without causing appreciable strain in the Ge surface. Rowe has pointed out that the adsorption site with three nearest neighbors is not an unreasonable choice for the Ge(111) surface which is more metallic than that of Si.¹⁴ Schlüter have reported that their theoretical calculation for chlorine chemisorption on Ge(111) favors the interstitial site over the covalent site.¹³

Based on these arguments we suggest that the CO molecule occupies an open site at the center of the surface triangle formed by three top layer Ge atoms,

with the carbon atom toward the bulk and the oxygen atom toward the vacuum, as shown in Fig. 7. Further discussion on the adsorption geometry of CO on Ge(111) must await theoretical study.

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