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Benzene adsorption on low-temperature silicon: A synchrotron-radiation photoemission study of valence and core states

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We present a synchrotron-radiation photoemission study of the different adsorption states for benzene on cleaved Si(111) substrates at room temperature and low temperature. The results provide information on the chemisorption or physisorption nature of the adsorption states. In particular, the data suggest that physisorption and chemisorption states coexist at low temperature and low coverage.

I. INTRODUCTION

A series of experiments revealed several unexpected chemisorption properties of benzene on cleaved Si(111).[1-3] These include a unique high reactivity at room temperature, the formation of C—Si σ bonds after breaking C—H bonds, and a chemisorption geometry with the molecular plane tilted with respect to the substrate. For comparison, the reactivity of benzene is extremely low on other semiconductor substrates including annealed Si(111). Benzene does chemisorb on room-temperature metals, but it forms bonds through a π-donor mechanism, resulting in a geometry with the molecular plane parallel to the surface. The high reactivity of benzene on cleaved silicon appears related to the cleavage steps.

Experimental evidence for the above properties was obtained with high-resolution electron-energy-loss spectroscopy[2] (HREELS) and synchrotron-radiation photoemission spectroscopy. Recently, these results were corroborated by a HREELS study of the temperature dependence of the absorption of benzene on cleaved Si, in the range 85—300 K.[3] The photoemission experiments described here expand the study of this temperature dependence, in the range 60—300 K. The results indicate, in particular, that chemisorption and physisorption states coexist at low temperatures. This fact was not revealed by the HREELS data, and provides further support for the hypothesis that the surface defects play an important role in establishing the stable chemisorption state.

Besides revealing new properties, the photoemission experiments also clarified the nature of temperature-dependent phenomena which had been revealed by HREELS experiments. The stable chemisorption state dominates adsorption at temperature of 135 K or even lower, depending on the quality of the cleaved surface. At 85 K, we found instead that the prevailing adsorption states are physisorption states. Three different physisorption states were observed for increasing benzene exposure. These three states correspond to isolated benzene molecules adsorbed with their plane parallel to the Si surface, to benzene clusters, and to benzene multilayers.[3]

The prevalence of a physisorption state at low temperatures and low exposures is confirmed by the low-coverage 60-K photoemission spectrum, which exhibits benzene molecular orbitals at energies similar to those of the free benzene molecule. The photon polarization dependence of this spectrum is consistent with the hypothesis of a "parallel" physisorption geometry. The C 1*s* core peak, however, indicates that at low temperature and low exposures the prevailing physisorption state coexists with a chemisorption state. At 60 K and exposures greater than 50 L (1 L = 10^{-6} Torr sec^{-1}) the photoemission spectrum is similar to the multilayer benzene spectra observed on metal surfaces,[4-8] which thus appear quite independent of the substrate.

II. EXPERIMENTAL PROCEDURE

The experiments were performed on *in situ* cleaved silicon, under ultrahigh vacuum (pressure in the low 10^{-10}-Torr range). The details of the benzene exposure procedure at low and room temperatures coincide with those reported in Refs. 1 and 3. In this case, the sample was cooled with a closed-cycle He refrigerator, thermally connected to the sample holder with a copper braid. The temperature was measured with a chromel-alumel thermocouple in contact with the sample.

Photoemission spectra were taken using a double-pass cylindrical mirror electron energy analyzer. The photons were emitted by the new 1-GeV storage ring of the University of Wisconsin Synchrotron Radiation Center (SRC). The experiments were performed at the 032 Wisconsin-General Motors beamline of SRC, equipped with a Brown-Lien Extended-Range Grasshopper (ERG) monochromator. Such a monochromator is a grazing-incidence Rowland-circle grating instrument with fixed exit slits. The beamline provides good output and excellent resolution for photon energies from 20 to 1200 eV. This enabled us to extend the experiments to the C 1*s* core level.

The polarization dependence of the spectra was studied by rotating the sample collinearly with the analyzer. We took spectra for two polarizations, one with the electric vector of the radiation parallel to the sample surface (pure *s* polarization), and the second with such a vector at an angle of ~45° with respect to the surface (mixed $s+p$ polarization).

III. RESULTS AND DISCUSSION

A. Valence electrons

A first series of photoemission experiments was performed on cleaved Si(111) at 60 K. Then we compared these low-temperature spectra with spectra taken at room temperature, using a much more extended range of photon energies than that of Ref. 1. In Fig. 1 we show two valence-electron spectra taken at 60 K for 5- and 100-L benzene exposures, and a third spectrum obtained with room-temperature exposure.

The room-temperature spectrum exhibits nine features. All of these features except peak *G* correspond to features reported in Ref. 1, and were interpreted as follows. Peaks *A* and *B* are related to chemisorption bonds involving silicon electrons. The remaining peaks correspond to benzene molecular orbitals. The ninth peak *G* was not previously observed due to the limited photon energy range.[1] Furthermore, improved resolution enabled us to emphasize the fine structure of peaks *E* and *C* of Ref. 1, which in Fig. 1 correspond to the features C',C'' and E',E''. The C',C'' fine structure is very important, since it is a fingerprint of the process whereby the benzene moleucle loses one hydrogen atom and forms a σ bond with a silicon surface atom.[1] Table I shows the correspondence between the chemisorbed-benzene molecular features of the room-temperature spectra and the molecular features of gas-phase benzene.[9] Notice that the chemisorbed-benzene positions reported in Table I are referred to the top of the Si valence band. These positions coincide within the experimental uncertainty with those we reported in Ref. 1, except for peak *F* which was barely visible in previous experiments, and for which we now have a much more reliable position estimate.

The exposure of freshly cleaved Si(111) at 60 K to benzene produces an attenuation of the clean-Si spectral features and new peaks related to the benzene molecular orbitals. At large exposures (middle curve in Fig. 1), the spectrum converges to that of multilayer benzene adsorbed on metal substrates.[4-8] The fact that the Si surface is completely covered for exposures greater than or equal to 100 L is consistent with the results of HREELS. However, in the present experiment we found that by lowering the temperature from 85 to 60 K complete cov-

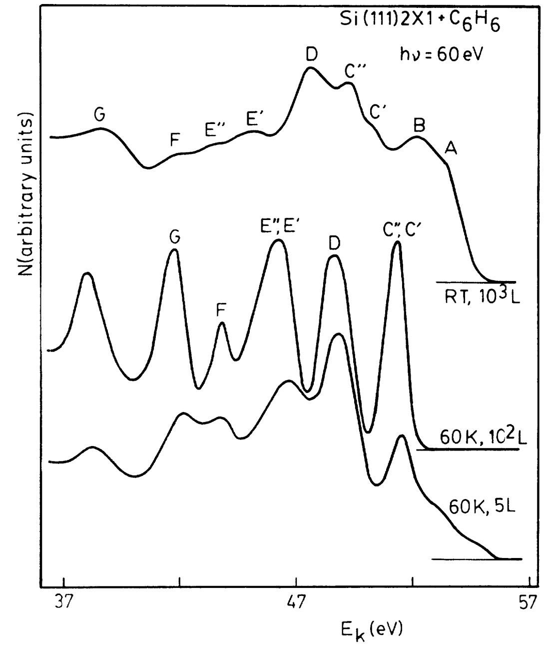

FIG. 1. Valence-electron photoemission spectra taken (from bottom to top) for cleaved Si(111)2×1 exposed to 5 L and 10^2 L of C_6H_6 while at 60 K, and exposed to 10^3 L of C_6H_6 while at room temperature (RT). The spectra were taken with a photon energy of 60 eV. The horizontal scale is the kinetic energy as measured with the electron energy analyzer. The labeling of the features for the top spectrum follows the convention of Ref. 1, and is discussed in the text.

TABLE I. Correspondence between photoemission spectral features of gas-phase benzene (from Ref. 9) and of benzene on Si(111)2×1 at room temperature. The positions are in eV, measured from the valence-band edge in the case of chemisorbed C_6H_6. The free-C_6H_6 molecular orbitals are identified in parentheses. Likewise, the photoemission peaks are identified in parentheses for chemisorbed benzene. As discussed in the text, peaks *A* and *B* observed for chemisorbed benzene on Si(111)2×1 are related to Si valence electrons affected by the chemisorption process rather than to molecular benzene orbitals.

Free C_6H_6	C_6H_6 on Si(111)2×1 at room temperature
	2.3 (*A*)
	3.7 (*B*)
9.3 ($1e_{1g}$)	5.3 (C'), 6.2 (C'')
11.8 ($3e_{2g}$), 12.5 ($1a_{2u}$)	8.1 (*D*)
14.0 ($3e_{1u}$), 14.9 ($1b_{2u}$), 15.5 ($2b_{1u}$)	10.7 (E'), 12.4 (E'')
17.0 ($3a_{1g}$)	13.8 (*F*)
19.2 ($2e_{2g}$)	16.6 (*G*)

erage could be obtained for lower exposures, ~50 L.

There are clear differences between the positions in energy of features related to benzene molecular orbitals in the room-temperature and low-temperature spectra. In order to compare these positions for the two temperatures, as well as with those for gas-phase benzene, we adopted the common practice of aligning in energy the features corresponding to $\sigma_{\text{C-C}}$ states, which are likely to be the least affected by adsorption processes.[4] For benzene on low-temperature Si(111) there is only one $\sigma_{\text{C-C}}$-related feature, peak E',E'' in Fig. 1. Using its position as zero for the energy scale, we derived the peak positions shown in Table II. For free benzene and for benzene on room-temperature Si(111), we adjusted the zero of the energy scale to coincide with the average of the positions of the $\sigma_{\text{C-C}}$-related peaks.

The resulting alignment is shown in Fig. 2. Notice that the alignment is quite good for all features when comparing C_6H_6 on low-temperature Si and free-molecule benzene.[9] This is additional evidence that the prevailing adsorption state at low temperature is a physisorption state with weak van der Waals bonds. Furthermore, we see that the C',C'' doublet observed on room-temperature substrates corresponds to a single peak on low-temperature substrates. This indicates that no breaking of the C—H bonds takes place at low temperature.

When comparing in Fig. 2 the free-benzene and physisorbed-benzene spectral features with those of benzene on room-temperature Si(111), we find significant shifts for the states with σ character, i.e., $2e_{2g}$ and $3e_{2g}$. The $2e_{2g}$ level is shifted by 0.5—0.6 eV to higher binding energies for the room-temperature substrate, while the $3e_{2g}$ peak (which also overlaps the $1a_{2u}$ contribution) exhibits a smaller shift to lower binding energies. This indicates that the $2e_{2g}$ and $3e_{2g}$ states are directly involved in the formation of chemisorption bonds at room temperature. Since the states have σ character, this confirms that C_6H_6 forms σ bonds with Si at room temperature. Such an experimental finding is in sharp contrast with the results for benzene chemisorbed on metals, e.g., Ni,[10] Pd,[10,11] and Pt.[12] For these, the π orbitals rather than the σ orbitals were found to shift to higher binding energies with respect to the free C_6H_6 molecule, indicating the formation of π bonds with the substrate.

We deduced from HREELS data that benzene is physisorbed on low-temperature Si with the molecular plane parallel to the substrate.[3] To test this conclusion, we took the 60-K, 3-L photoemission spectra with different photon polarizations, i.e., pure s polarization and mixed $s+p$ polarization. The two spectra are shown in Fig. 3.

TABLE II. Energy positions in eV of the molecular-orbital features for C_6H_6 adsorbed on Si(111)2×1 at 60 K. The zero of the energy scale is defined in the text.

C_6H_6 molecular orbital	Position
$1e_{1g}$	5.1
$3e_{2g}+1a_{2u}$	2.4
$3e_{1u}+1b_{2u}+2b_{1u}$	0.0
$3a_{1g}$	−2.4
$2e_{2g}$	−4.4
$2e_{1u}$	−8.1

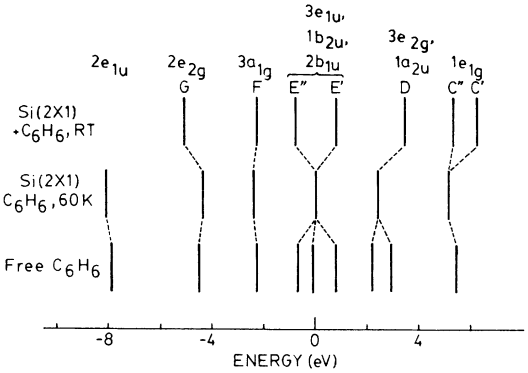

FIG. 2. Position in energy of the spectral features for gas-phase benzene and for chemisorbed benzene on cold and room-temperature substrates. We adopted here the convention of aligning the $\sigma_{\text{C-C}}$ features, which should be the least affected by the adsorption processes.

Notice that the relative intensity of peak C',C'' (i.e., the $1e_{1g}$ feature) is much lower for s polarization than for mixed polarization. This is consistent[13] with the hypothesis that the prevailing orientation for the corresponding C $2p$ orbitals which form the benzene π system is in the direction perpendicular to the substrate. In turn, this orientation is consistent with a "parallel" adsorption geometry.

B. Core electrons

Photoemission spectra were taken for the Si $2p$ and C $1s$ core levels for room-temperature and 60-K substrates. The Si $2p$ peak position does not significantly change with

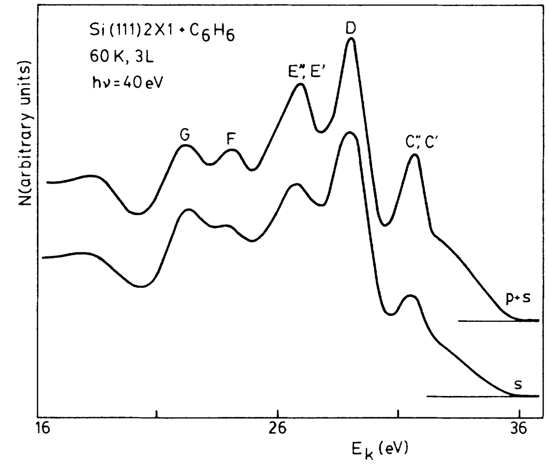

FIG. 3. Photon polarization dependence of the $h\nu=40$ eV photoemission spectra for low-temperature Si(111)2×1 exposed to 3 L of benzene. The polarization is pure s for the lower curve and mixed $p+s$ for the upper curve, as discussed in the text.

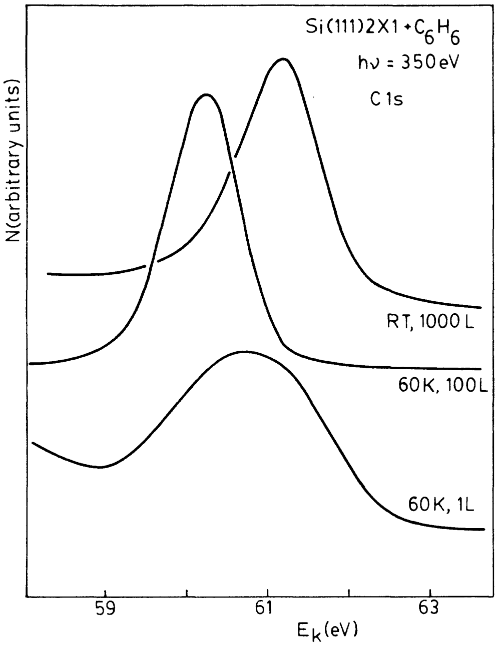

FIG. 4. C 1s core-level photoemission spectra taken with a photon energy of 350 eV for low-temperature Si(111)2×1 exposed to 1 and 100 L of C_6H_6, and for room-temperature Si(111)2×1 exposed to 10^3 L of C_6H_6.

the substrate temperature. The formation of multilayer benzene at low temperature and high exposures is reflected in the progressive attenuation of the peak.

Figure 4 shows C 1s spectra taken at 60 K for 1- and 100-L exposures, and for saturation coverage at room temperature. For low temperature and low coverage, the peak is broad, with full width at half maximum (FWHM) ~1.9 eV. This indicates that the peak contains at least two components. As the exposure increases, the high-binding-energy component prevails, giving a narrower peak with FWHM ~1 eV. This last peak is likely to correspond to only one chemical environment for the C atoms.

At room temperature, for which the chemisorption state prevails, the peak is also narrow, with FWHM is ~1.2 eV. The kinetic energy is 0.5 eV higher than at low temperature and high coverage. Quite interestingly, the low-temperature, low-exposure peak seems to correspond to an overlap of the other two peaks. This suggests that the chemisorption state is present together with the physisorption state after low exposure of the low-temperature substrate. Only after substantial exposure to benzene does the chemisorption signal disappear.

The presence of chemisorbed benzene even at low temperature is quite intriguing. It indicates that the chemisorption sites are active at all temperatures in the range explored here. Together with the HREELS data which indicate a dependence of the reactivity on the cleavage quality,[3] this is additional evidence that the formation of the unusual, strongly bound chemisorption state is activated by special sites, presumably related to cleavage steps.

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