Photoelectron Diffraction Imaging for C_2H_2 and C_2H_4 Chemisorbed on Si(100) Reveals a New Bonding Configuration

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A new adsorption site for adsorbed acetylene on Si(100) is observed by photoelectron imaging based on the holographic principle. The diffraction effects in the carbon $1s$ angle-resolved photoemission are inverted (including the small-cone method) to obtain an image of the atom's neighboring carbon. The chemisorbed acetylene molecule is bonded to four silicon surface atoms. In contrast to the C_2H_2 case, the image for adsorbed C_2H_4 shows it bonded to two Si surface atoms.

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In a surprising contradiction to the existing literature, the adsorption site for acetylene at saturation coverage was observed to be different from that of ethylene. The adsorption sites for chemisorbed ethylene, C_2H_4, and chemisorbed acetylene, C_2H_2, on the (100) face of silicon have been directly observed using photoelectron holographic imaging. In this recently developed technique, photoelectron diffraction intensities are measured and then inverted, to directly obtain the local three-dimensional environment of the emitting atoms [1,2]. The small-cone inversion technique is used [1]. This study is believed to be the first photoelectron holographic study of a multiatomic adsorbate. No model calculations were used in the adsorption site determination. An understanding of the bonding of the ethylene and acetylene molecules provide a foundation for understanding the adsorption behavior of complex unsaturated organic molecules. The carbon-carbon double bond or triple bond in a hydrocarbon molecule may be used to "fasten" the molecule to the Si(100) surface. Such molecules could have a broad range of functions, which have interesting and important applications [3]. Such species are also important in the science of carbide formation.

The ethylene adsorption site found here agrees with the previously reported site, but the acetylene adsorption site was determined to be different. Identical adsorption sites for the two molecules have been reported based on the results of high-resolution electron-energy-loss spectroscopy [4], photoemission spectroscopy [5], scanning tunneling microscopy [6], and near-edge x-ray-adsorption fine structure (NEXAFS) [7], and also in theoretical studies [8]. The experimentally determined image for adsorbed C_2H_4 shows it bonded to the dangling bond of two silicon surface atoms. In contrast, the image for adsorbed C_2H_2 shows bonding to four silicon surface atoms, while retaining one C-C type bond as does chemisorbed C_2H_4.

Photoelectron diffraction occurs when the direct wave from an emitter (carbon) interferes in the far field with a wave from the scatterers (silicon). The method of obtaining an image from the data has been published [1]. The angle-resolved emission strength for the emitter's core level of interest is measured for a range of incident photon energies. Since the initial energy for the core level is a constant, the resultant spectrum is a constant-initial-energy spectrum (CIS) [9]. Representative CIS spectra are shown in Fig. 1. The first step is the separation in the CIS spectrum, $I_{\hat{k}}(k)$, of the diffractive portion from the background, $I_{\hat{k}0}(k)$, and an example background (dotted line) is shown. The diffractive portion of the experimental spectrum is extracted using $\chi_{\hat{k}}(k) = I_k(k)/I_{\hat{k}0}(k) - 1$. EXAFS uses a similar χ function and the present method may be called vectorized EXAFS. The data are inverted to obtain an image function [10]:

$$U(\mathbf{R}) = \left| \sum_{\hat{k}} \int_{k_{\min}}^{k_{\max}} \chi_{\hat{k}}(k) e^{-ikR(1-\hat{k}\cdot\hat{R})} \, dk \right| . \quad (1)$$

The inversion is based on the holographic principle and $\mathbf{R}$ denotes a direct-space position vector with its origin at the emitter. It is important to first do the transform against wave numbers. The small-cone method is used in the sum over the angles which minimizes artifacts [1]. The position of a given atom is given by the local maximum in $U(\mathbf{R})$ and its centroid is used in the determination of interatomic distances. The precision of the numerical results may be distorted by as much as one- or two-tenths of an angstrom [1,2,10].

Strictly speaking, the wave from each of the numerous emitters on the surface forms an internal-source holographic image. The atomic image obtained comes from many reference waves. Each emitter's signal is incoherent with respect to the other emitters, so the image intensities from each emitter are summed by simple addition. The image resulting from each individual emitter, however, has the same origin in the inverted aggregate image, so the expression "holographic image" is a more liberal usage of the term. In the case of a single site adsorbate, where each adsorbate emitter atom has an identical local geometry, the assignment of peaks in the image is straightforward. When
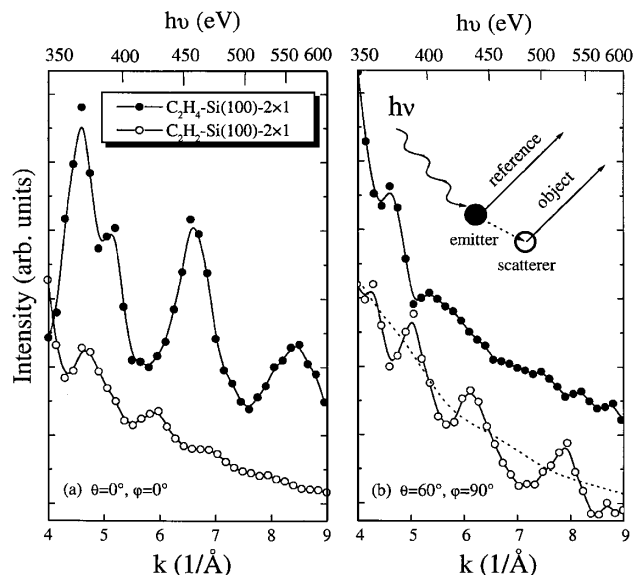
FIG. 1. Photon-energy dependent CIS of the C $1s$ emission strength from C_2H_4 and C_2H_2 adsorbed on Si(100) where the lower axis is the electron's wave number and the upper is photon energy proportional to the wave number squared. The emission directions are in polar coordinates; $\theta = 0$ is normal emission. The interference effects are different for the two species with the immediate implication that each is in a different adsorption site.

there are two emitters in inequivalent adsorption sites, the resultant image for the pair of atoms is akin to a double-exposed photograph. The atomic structure may be obtained through reduction of the image by examination of the image in light of other information regarding the molecular structure of the adsorbate, the bulk crystal structure of the substrate, etc. This is important for the present study since both of the chemisorbed species have two carbon-atom emitters with the carbon atoms in inequivalent locations in the surface unit cell. If some of the adsorbed molecules were in different adsorption sites, they also would make their additive contribution to the experimental image. If the concentration of these molecules were small, it would be difficult to differentiate their image features from artifacts associated with the image of the molecule in the dominant adsorption site.

The Si(100) surface is reconstructed and composed of rehybridized silicon atoms referred to as dimers. Each atom of the dimer pair also has a dangling bond which is very reactive. The surface structure is 2×1 and a single domain stepped surface is obtained when the Si substrates are miscut by $\sim 3.5°$. The adsorbate coverage was near saturation for both cases. Low-energy electron diffraction was used to determine the direction of the step edge and the direction of the dimer bond.

The data were collected at beam line 7 at the Advanced Light Source at the Lawrence Berkeley Laboratory, one of only a couple of beam lines that can do this imaging. Incident photon energies of $\sim 350–600$ eV were used to probe the C $1s$ core level corresponding to a range in wave number k of $\sim 4–9$ Å^{-1}. About 80 CIS were collected

on a grid covering one-fourth of the emission hemisphere, which is an irreducible symmetry element of the surface.

To facilitate the presentation of the experimental images, three-dimensional ball-and-stick models of the determined adsorption sites for C_2H_4 and C_2H_2 are shown in Fig. 2. The balls are arranged according to the directly determined atomic locations, except for H which is not detected. In the case of ethylene, carbon atoms in the molecule sit above the surface silicon dimer so that the C-C bond and the Si-Si bond axes are parallel; the bar represents the dimer bond. In the case of acetylene, the carbon atoms in the molecule sit between two silicon dimer pairs, above the dimer plane.

A planar vertical cut from the experimental image function $U(X, Y, Z)$ obtained for the chemisorbed ethylene species is shown in Fig. 3. To aid in recognizing the individual atoms, the cut is accompanied by a ball-and-stick construction for the image. When viewing the experimental image function, it is important to realize that the emitter does not see itself but is always located at the origin $(0, 0, 0)$ of the three-dimensional image. The double peak, Si(1), is observed and corresponds to the first layer silicon atoms. The lower-intensity features located between the origin and the first layer Si peaks are attributed to artifacts.
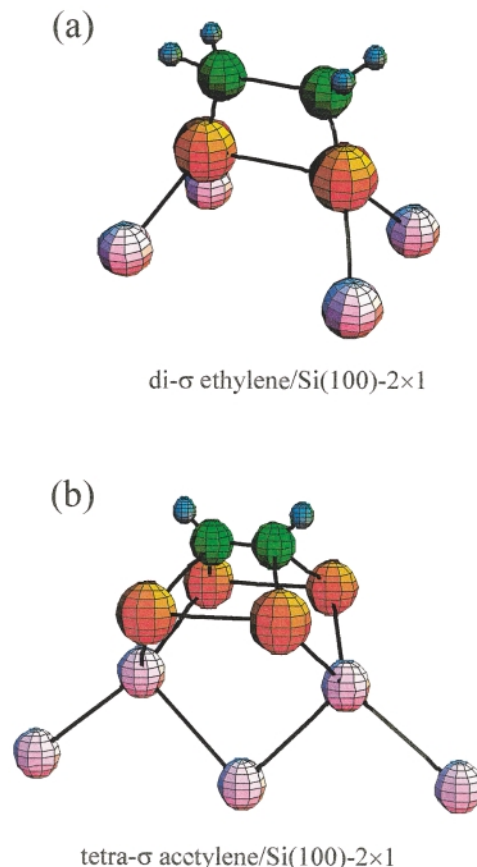

FIG. 2 (color). Ball-and-stick sketches of the Si(100) adsorption sites for (a) C_2H_4 and (b) C_2H_2 showing two and four Si neighbors, respectively. The big green balls: C; the orange balls: first layer Si; the pink balls: second and third layer Si. The small green balls added in the likely positions for the H atoms.
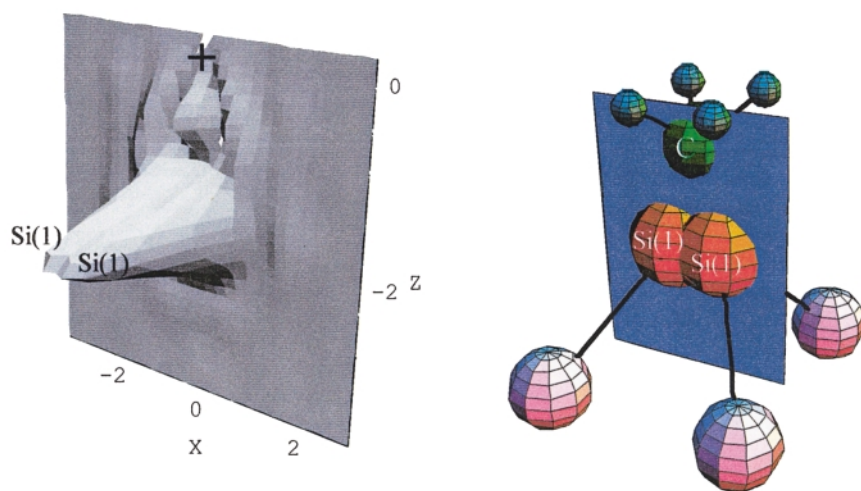
FIG. 3 (color). Vertical X-Z cut at $Y = 0$ through the chemisorbed C_2H_4 image function whose intensity is in the third dimension. Both carbon emitters are at the origin, marked with a "+" sign. X is the Si-Si dimer direction. The image has to be reduced to get the atomic structure in Fig. 2(a). The image shows a strong doublet for two first-layer silicon atoms (depth 1.8 Å and horizontal separation 0.6 Å) whose actual separation is that observed in the image plus the C-C separation (see text).

To relate to the earlier ball-and-stick model of the atomic structure in Fig. 2(a), consider that the ball representing the carbon emitters is not one atom but two superimposed carbon atoms. Now imagine shifting the carbon balls in Fig. 2(a), representing the emitting carbon atoms of the atomic-model sketch, towards each other along the line joining them, until they coincide. The resulting ball-and-stick construction is that shown with the image in Fig. 3. This shift represents the C-C bond length. Note that the separation (0.6 Å) in the double peak is not an interatomic distance but is the difference between the C-C bond length and the Si-Si dimer bond length [11].

A preview of the chemisorbed acetylene result is given before the image is discussed. Its interpretation is more involved since $U(\mathbf{R})$ shows peaks for atoms in the second and third layers. First, it is shown that the C_2H_2 chemisorption site is such that the molecule does not sit directly over the first layer Si atoms. Instead the molecule is over the second and third layer Si atoms which by virtue of the crystal structure means that the C_2H_2 adsorbed molecule has four Si atoms for neighbors in the first layer. Second, the image contains a third layer Si(3) atom signal that allows one to reduce the double image and to obtain a value for

the C-C bond length as well as the first layer Si-Si distance [11].

Figure 4 shows a vertical cut from the chemisorbed acetylene image. The strongest features in $U(\mathbf{R})$ are the two peaks located under the emitters at $Z = -1.6$ Å which are due to the second layer Si(2) atoms. The third layer silicon atoms Si(3) at $Z = -3.0$ Å also have quite evident peaks. The image clearly shows that the carbon emitters are in the vertical plane containing the second and third layer atoms, which means they are not "directly" above the first layer Si atoms. Presumably, this is why the carbon emission is strongly scattered by the deeper Si atoms. In a manner analogous to the above C_2H_4 image discussion, separation of the carbon atom in the ball-and-stick *image* construction shown in Fig. 4 will give the ball-and-stick atomic structure *model* shown in Fig. 2(b). The most important finding is that the acetylene molecule has four first layer Si atoms as nearest neighbors (two Si dimers).

A curious and significant feature due to the "double exposed" nature of the image allows a determination of the C-C distance for adsorbed C_2H_2. The twin peak at $Z = -3.0$ Å is actually due to a SINGLE silicon atom Si(3) in the third layer of Si atoms. In the image, this atom
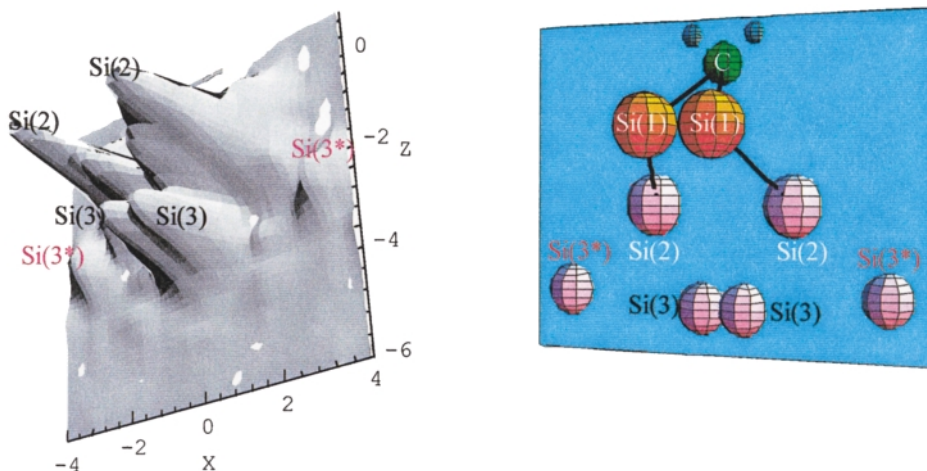

FIG. 4 (color). Vertical planar X-Z cut at $Y = 0$ through the chemisorbed C_2H_2 image function whose intensity is in third dimension. The carbon emitters (origin) are in the plane. The two strong peaks in the image are second-layer Si(2) atoms and just below them are the peaks for third-layer Si(3), where Si(2) and Si(3) have vertical depths of 1.6 Å and 2.8 Å, and horizontal separations of 3.0 Å and 1.1 Å, respectively. X is the dimer direction.

is being "seen" by both of the inequivalent carbon emitters in the molecule but each emitter's image has the same origin so Si(3) appears twice in the image. As discussed above for the relationship between the ball-and-stick constructions for the image and for the atomic-structure model, one can imagine collapsing the carbon atoms in Fig. 2(b) along their bond direction until the carbon atoms are superimposed. This manipulation makes two balls from the single ball that represents the third layer Si atom Si(3) in Fig. 2(a). The image shows two such peaks and their distance of separation of 1.2 Å gives the interatomic distance between the two carbon emitters in the adsorbed C_2H_2 molecule. That is, the image itself (Fig. 4) contains the numerical information needed to reduce the double exposed image to the atomic structure [Fig. 2(b)] [12].

Now, examine the strongest image peaks in Fig. 4 due to the second layer Si atoms. The true interatomic distance (reduced image) between the second layer Si atoms is the sum of the distance between the peaks, Si(2), in the image, 2.8 Å, plus the 1.2 Å needed to reduce the double exposed image. The sum of 4.0 Å is close to bulk the Si-Si distance of 3.84 Å and forms a consistency check.

Having experimentally determined the adsorption site, the bonding models are considered. For C_2H_4 and C_2H_2, sp^2 and sp hybridization of carbon exists. The remaining p-like states form π bonds that do not lie on the molecular axis. The chemisorption is then viewed as the severing of a π orbital allowing for bonding to the dangling bonds of the dimer atoms. The new bonds have sigma character. Pauling presents an equivalent description, the bent bond picture, in which each carbon atom tends to form tetrahedral sp^3-like orbitals [13]. In the free ethylene and acetylene molecules, bent (and strained) bonds form between the two carbons giving the ethylene a C-C double bond and the acetylene a C-C triple bond. Hence, on chemisorption the "bent bonds" simply open up and attach to the dangling bonds on the silicon surface atoms, which leaves just a single bond between the carbon atoms in each case. Thus from the initial hybridization states in each molecule, the chemisorbed form adopts a sp^3 carbon hybridization and a surface "alkane" species forms in each case. There is an interesting comparison between the C_2H_4 and C_2H_2 surface complexes since they can be viewed as surface molecules $C_2H_4Si_2$ and $C_2H_2Si_4$ suggesting a similarity between the C-H and C-Si bonds. In thermal breakdown, it is known that C_2H_4 is liberated in the one case, and for the other C_2H_2 decomposes forming a carbide [14]. The latter complex stays on the surface, probably because it has two bonds for each carbon while the C_2H_4 case forms only one bond. The analysis of the line shape for the high-resolution core-level-photoemission peaks supports the assignments made here [15], as does the observed vibrational frequency [16].

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[11] The images that show weak spots due to one carbon atom's emission scattering from the other carbon atom of the molecule will be presented elsewhere. For C_2H_2 the separation of these spots is 1.1 Å in agreement with the 1.2 Å value observed for the third layer silicon. For C_2H_4 the separation is 1.6 Å. These values give, respectively, 2.2 and 2.3 Å for the Si-Si dimer bond length in the surface complex which compares to 2.23 Å for the clean surface. Apparently, the adsorption does not break the dimer bond.

[12] The first layer results from the acetylene image, to be presented elsewhere, give an interplanar separation between the adsorbed C and first layer Si of 0.8 Å and a Si-Si dimer length of 2.3 Å. The C-Si distance is 1.8 Å and for C_2H_4 the observed value is 2.2 Å which compares to the 1.89 Å. For bulk SiC the bond length is 1.89 Å.

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[16] The vibrational spectrum for chemisorbed C_2H_2 is in agreement since it shows a C-C frequency, 1040 cm^{-1}, very near to that known for single C-C bonds, 950 cm^{-1}. See Ref. [4].