

Three-Dimensional Atomic Images of As/Si(111) Obtained by Derivative Photoelectron Holography

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The atomic structure of As-terminated Si(111) is imaged by a new technique of photoelectron holography based on differential measurements. The improved sensitivity of this technique allows second nearest neighbors to be detected. Images deduced from both the As and the Si core level emission provide a detailed three-dimensional view of the bonding structure involving the top three atomic layers. The results provide direct evidence for As replacement of the top Si atomic layer. [S0031-9007(98)07640-6]

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Photoelectron holography has emerged as a powerful tool for surface structural determination [1–11]. Its strength lies in its ability to provide a three-dimensional view of the local atomic structure by direct data inversion. This is contrasted by traditional diffraction methods, which must rely on presumed (and possibly incorrect) models for data analysis. Although the power of photoelectron holography has been widely recognized, its application has been rather limited due to various technical issues that will be discussed below. The present study is an application of a new technique of photoelectron holography to the As-terminated Si(111) surface. This system is widely regarded as a prototypical adsorbate system, and essentially all available surface science tools, both experimental and theoretical, have been employed to gather information about the atomic structure [12–22]. It is generally believed that the structure is basically a bulk truncated Si(111) with its top monolayer replaced by As in a simple (1×1) geometry. Each As atom, with five valence electrons, is triply coordinated to the Si substrate, leaving a nonbonding pair on the As. Although there is considerable support for this model, the experimental evidence is essentially all based on *indirect* methods. Given the high degree of interest in this system as a test case for basic concepts of adsorption, it is important that a direct determination of the structure be made. The present study is a holographic analysis of photoemission data taken from the As $3d$ core level and the chemically shifted Si $2p$ core level. The use of both core levels in conjunction with a derivative method (see below) allows a detailed analysis of the atomic bonding structure of the top three atomic layers. The resulting images show atoms as well defined intensity maxima with little spurious contributions from noises, twins, and ghosts, which are often problems encountered in previous holographic studies of related systems. These images provide direct confirmation of the model described above.

In traditional photoelectron holography experiments, the emission intensity of a core level $I(h\nu, \hat{\mathbf{k}})$ is measured over a wide range of photon energy $h\nu$ for a number of emission directions $\hat{\mathbf{k}}$. The measured intensity shows variations (oscillations) on the order of 10% due to diffraction effects, which carry the desired structural information. A function characterizing these oscillations can be extracted from the data by first subtracting a smooth background function $I_0(h\nu, \hat{\mathbf{k}})$ and then normalizing to it:

$$\chi(\mathbf{k}) = \frac{I - I_0}{I_0}, \quad (1)$$

where \mathbf{k} is the photoelectron momentum. The holographic transform that yields the atomic images is given by a Fourier-like transform of the χ function:

$$U(\mathbf{r}) = \left| \iiint \chi(\mathbf{k}) \exp[i\mathbf{k} \cdot \mathbf{r} - ikr] g(\mathbf{k}) d\mathbf{k} \right|^2, \quad (2)$$

where $g(\mathbf{k})$ is a window function.

The method is straightforward. The main difficulty here is related to data uncertainty. As mentioned above, χ is on the order of 10%. To deduce the atomic structure reliably, this function must be measured accurately with a random error of no more than $\sim 10\%$. Thus, each photoemission intensity measurement must be reproducible to within $\sim 1\%$. This is often difficult to achieve. A typical data set may involve thousands of data points covering a wide photon energy range, and it is necessary to change monochromator gratings and slit settings for measurements in different energy ranges. Intensity renormalization must be carried out in order to splice together different pieces of data, which introduces error and requires additional control data and experimental time. Another problem is related to the need to refresh the sample from time to time, which may involve sample transfer for sputtering, annealing, deposition, and characterization. It

is extremely difficult to reproduce measured intensity at the 1% level after each sample preparation and manipulation, as any experienced surface scientist can attest to. These problems have significantly affected our ability to implement the holographic method for routine work. Previous holographic studies of related systems have generally yielded images of first nearest neighbors only (as diffuse and sometimes distorted objects on a noisy background), but a definitive structural determination often requires information about more distant neighbors. Signals from more distant neighbors are much weaker due to attenuation by inelastic scattering, and are particularly sensitive to uncertainty and noise.

To circumvent this problem, we have developed a new method for the present study of As/Si(111). A key feature of this method is intensity self-normalization, and the advantages are a simplified experimental procedure and much improved image quality including the observation of second nearest neighbors. Instead of measuring $I(h\nu, \hat{k})$ directly as discussed above, we make a differential measurement involving two spectra related by a small difference in photon energy 2δ . The result is a pair of data points, $I(h\nu - \delta, \hat{k})$ and $I(h\nu + \delta, \hat{k})$, from which we can calculate the logarithmic derivative function L :

$$\begin{aligned} L(h\nu, \hat{k}) &\equiv \frac{I'(h\nu, \hat{k})}{I(h\nu, \hat{k})} \\ &= \frac{I(h\nu + \delta, \hat{k}) - I(h\nu - \delta, \hat{k})}{[I(h\nu + \delta, \hat{k}) + I(h\nu - \delta, \hat{k})]\delta} \\ &= \frac{I(h\nu + \delta, \hat{k})/I(h\nu - \delta, \hat{k}) - 1}{[I(h\nu + \delta, \hat{k})/I(h\nu - \delta, \hat{k}) + 1]\delta}. \end{aligned} \quad (3)$$

Since this quantity depends on the ratio between the data points taken at nearly the same time without any changes in experimental settings, the error mentioned above is absent. For example, a change in monochromator slit setting can affect subsequent intensity measurements by a significant factor, which may not be precisely known. The same factor, however, affects both data points, and when the ratio is taken, its effect is canceled. Thus, values of logarithmic derivatives can be determined much more precisely, and data taken for different gratings, different slit settings, different analyzer pass energies, and even different monochromators can be joined together directly. Once the logarithmic derivative function is determined, it is straightforward to calculate the intensity function itself (apart from an unimportant integration constant):

$$I(k, \hat{k}) = \exp\left[\int L(k, \hat{k}) dk\right], \quad (4)$$

where the primary variable has been changed from the photon energy to the photoelectron wave vector k . The rest of the holographic inversion procedure is then the same as discussed above.

The As/Si(111) sample used in our experiment was prepared in accordance with recipes given in the literature [12–22]. A freshly prepared Si(111)-(7 × 7) was raised to 700 °C while exposed to As vapor for an equivalent dose of a few monolayers. This was followed by a brief postdeposition anneal. The As coverage saturated at one monolayer, and the resulting surface showed a (1 × 1) reconstruction as verified by reflection high energy electron diffraction. The photoemission measurements were carried out at the 1-GeV storage ring Aladdin at the Synchrotron Radiation Center (Stoughton, Wisconsin). The As 3*d* core level was measured, and each spectrum was fitted to Voigt functions to deduce the intensity. For each emission direction, 37 logarithmic derivatives evenly spaced in k within the range of $2.4 \text{ \AA}^{-1} < k < 6.4 \text{ \AA}^{-1}$ were determined. The procedure was repeated for a total of 44 different angles roughly evenly spaced over a polar angle range of 0° to 70° and an azimuthal angle range of 0° to 60° (zero azimuth corresponds to $[2\bar{1}\bar{1}]$). Threefold rotation and mirror symmetry operations expanded the effective number of angles to 238, corresponding to a total of over 8800 points in k space. A set of data was also taken from the Si 2*p* core level. The total beam time used for this experiment was two weeks.

Figure 1(a) shows a typical As 3*d* core level spectrum. The two peaks correspond to a spin-orbit splitting of 0.7 eV. Figure 1(b) shows a typical Si 2*p* core level

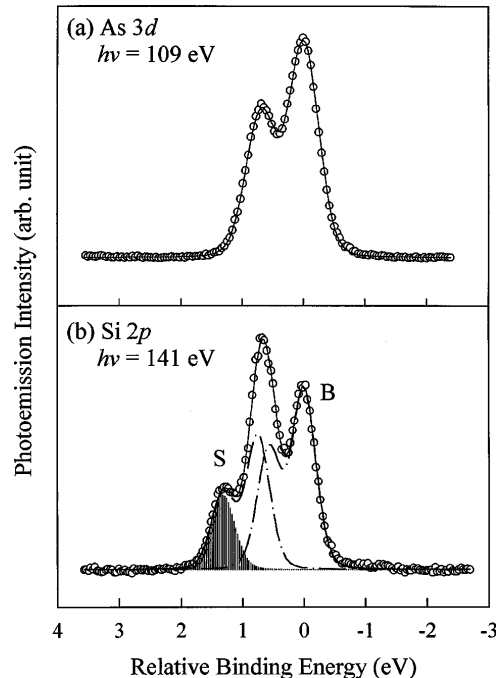


FIG. 1. (a) A typical As 3*d* core level spectrum. (b) A typical Si 2*p* core level spectrum and its decomposition into the bulk (B) and surface (S) components. The shaded area shows the 2*p*_{1/2} component of *S*, which is used in our holographic analysis. Both spectra were taken in normal emission, and the photon energies are indicated.

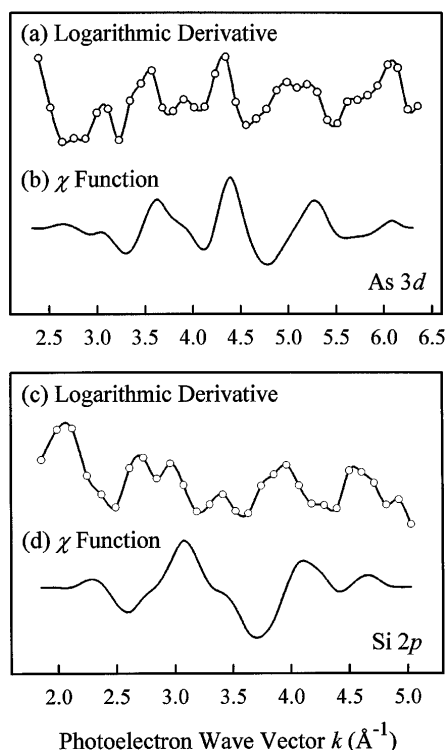


FIG. 2. (a) Logarithmic derivatives of the As $3d$ intensity as a function of photon energy for a polar angle $\theta = 30^\circ$ and an azimuthal angle $\phi = 46^\circ$; (b) the corresponding χ function; (c) logarithmic derivatives of the chemically shifted Si $2p_{1/2}$ intensity as a function of photon energy for $\theta = 30^\circ$ and $\phi = 47^\circ$; and (d) the corresponding χ function.

level spectrum and its decomposition into two components, each being a spin-orbit doublet with a splitting of 0.58 eV. The component at lower binding energy is derived from the bulk, and the chemically shifted component to higher binding energies is derived from Si bonded directly to surface As [12,19,21]. The intensities of individual peaks in the overlapping region deduced from the fit are less reliable, and therefore the intensity of the chemically shifted Si $2p$ used in our analysis includes the $2p_{1/2}$ component only (indicated by the shaded area in Fig. 1). Figure 2 shows typical logarithmic derivatives and the corresponding χ functions for the As $3d$ and the chemically shifted Si $2p_{1/2}$. The collection of χ functions is used in conjunction with Eq. (2) to construct real space images. The window function g used here is a product of a Welch function in k and an angular Gaussian with a width of $\pm 25^\circ$. This window function is included to suppress artifacts caused by the cutoffs corresponding to the finite k range and to limit the angular phase variation; the angular acceptance cone moves with the direction of integration (sweeping cone method) [2,11].

Figure 3 summarizes the holographic results. Shown on the right in Fig. 3 are ball-stick model drawings of the atomic structure. The top atom, colored red, is As, which is bonded to three Si atoms below forming a

tripod geometry. Each of these three Si atoms is in turn bonded directly underneath by a Si atom in the second layer. The panels on the left are planar slices through the three-dimensional holographic image function, and the slicing planes are as shown in the ball-stick model. Figure 3(b) is a horizontal slice through the three pedestal Si atoms bonded below the As emitter, and the image shows three intensity maxima corresponding to these atoms. The crosses are average atomic positions deduced from previous theoretical and experimental work [13–19], and are in good agreement with the image. Figure 3(c) is a slice through the three Si atoms in the second layer

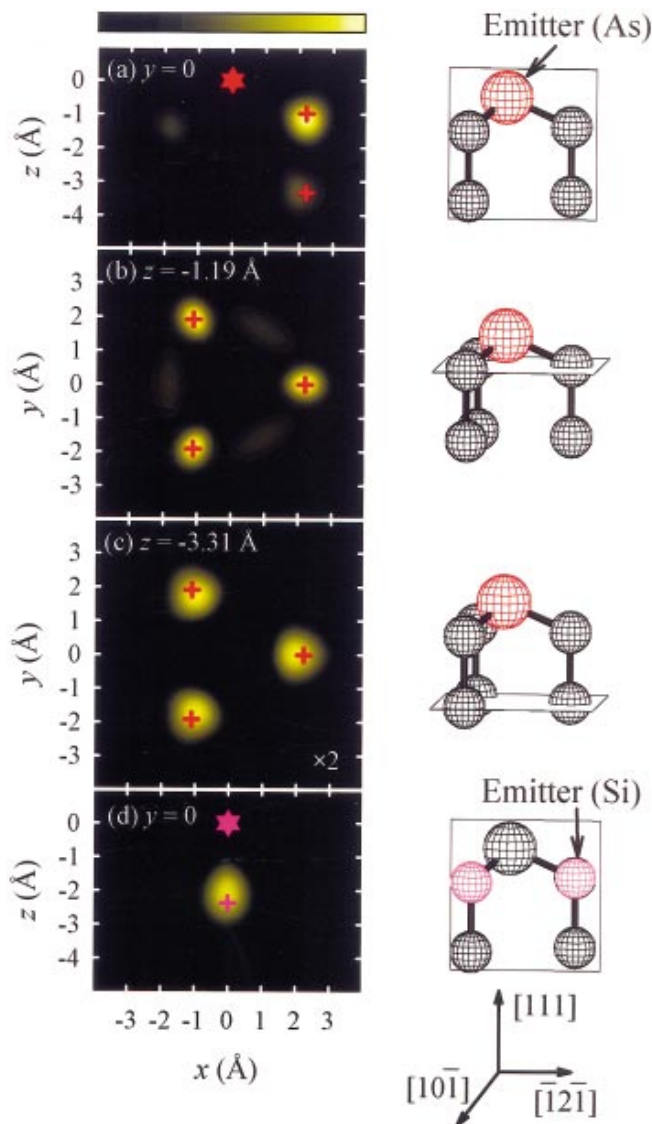


FIG. 3(color). Planar slices of the image function through various atomic planes as indicated in the accompanying ball-stick model drawings. The gray scales used for image presentation are indicated near the top of the figure by a linear mapping of the intensity levels into gray levels. (a)–(c) are obtained from the As $3d$ data, and (d) is from the Si $2p$ data. The intensity level of the image in (c) has been amplified by a factor of 2 to improve visibility.

(for easy viewing, the intensity level of this image has been amplified by a factor of 2). Again, the positions of the three intensity maxima are in good agreement with the accepted model as indicated by crosses. These intensity maxima are weaker than those seen in Fig. 3(b) because the farther distance from the As emitter results in a greater attenuation of the diffraction modulation by inelastic scattering. Figure 3(a) is a vertical slice through a plane containing $[111]$ and $[\bar{1}2\bar{1}]$. The position of the As emitter, also the origin of the coordinate system, is marked by a star. Here, one expects to see a Si pedestal atom to the lower right and a Si atom in the second layer, as indicated by the crosses. These are clearly seen in our image. It should be emphasized that most previous photoelectron holographic results for similar systems were able to detect only the first nearest neighbors as diffuse objects. Our observation of well-defined second nearest neighbors can be attributed to the improved experimental accuracy associated with the derivative technique.

Figure 3(d) shows a vertical slice of the image function deduced from the chemically shifted Si $2p$ core level. The emitting atoms are colored magenta in the accompanying model. In this case, one expects to see the Si atom bonded directly underneath, and this is indeed observed in our image. Careful inspection of the original data reveals that the second nearest neighbors are also present, but the intensity level is extremely dim and therefore not visible in Fig. 3. Taking the As and Si data together, the bonding structure for the top three atomic layers is verified in detail, thus confirming the model involving As replacement of the top Si layer. This would not be the case if we had images for the two top atomic layers only. For example, the often observed T_4 and the related H_3 adsorption sites on Si(111) also have the same local tripod bonding geometry, and the replacement site observed in this experiment can be distinguished only because the atomic positions in the third layer are known.

In summary, the atomic structure of As/Si(111), long regarded as a prototypical test case for basic concepts of semiconductor adsorption, has been determined directly by photoelectron holography. Both the As $3d$ and the chemically shifted Si $2p$ core levels are used in the analysis, and the atomic bonding configurations within the top three atomic layers are verified. The high quality of the atomic images can be attributed to a new holographic approach based on intensity self-normalization, which reduces data uncertainty and allows data taken under widely different experimental conditions to be analyzed together.

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