Photoelectron holographic studies of As/Si(100) with sub-angstrom resolution

Paul J. E. Reese, T. Miller, and T.-C. Chiang

Department of Physics, University of Illinois at Urbana-Champaign, 110 West Green Street, Urbana, Illinois 61801-3080
and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, 104 South Goodwin Avenue, Urbana, Illinois 61801-2902

(Received 6 June 2001; published 31 August 2001)

The atomic structure of As-terminated Si(100) has been studied using the technique of derivative photoelectron holography. The resulting holographic images clearly resolve a 0.5-Å shift from the (1×1) geometry for each As atom as a result of dimerization. Detecting this shift requires a sub-angstrom resolution that has been difficult to achieve using photoelectron holography. The improvement in resolution can be attributed to a highly anisotropic electron-scattering factor resulting in an emission beacon that helps define the atomic images.

DOI: 10.1103/PhysRevB.64.113409

Photoelectron holography is a direct, model-independent method for surface structural determination which is of fundamental importance to surface science. In the past, one disadvantage to many photoelectron holographic studies has been a limited resolution which makes it difficult to resolve atoms that lie near one another in the holographic image. For this reason, most such studies have been performed on relatively simple systems with a small number of imaged atoms or with little effort to resolve nearby atomic images. This severely limits the utility of the technique. The As/Si(001) system, with a two-domain dimerized surface structure, has a total of eight image atoms as first neighbors with pairs of image atoms lying 1 Å away from each other, or a mere 0.5 Å from the mirror plane which separates them. An effective study of this system would need to resolve this small length scale. Achieving the necessary sub-angstrom resolution is a challenge which is met by the present study. Sub-angstrom resolution for atomic imaging has been a critical issue and a long-term goal in the closely related field of transmission electron microscopy. Current state-of-the-art instruments offer a resolution of about 1.4 Å. This limits atomic-resolution studies to low-index orientations in simple systems, and many systems of practical importance are thus beyond the realm. A major new initiative within the U.S. Department-of-Energy National-Laboratory System is to develop and construct a next-generation, aberration-corrected instrument with a 1-Å resolution and below. This capability is critically needed for supporting the present multiagency national initiatives on complex systems and on nanoscale science, engineering, and technology.

There have been few systematic, detailed investigations of the resolution issue in photoelectron holography. Traditional simplified models of photoelectron holography have often assumed an effectively isotropic amplitude for the scattering of a photoelectron from nearby scatterers. Simulations of the As/Si(100) system using these models would suggest that it is impossible to successfully resolve image atoms separated by such short distances. To the extent that anisotropy in the scattering amplitude has been considered, it is usually invoked to explain problems with holographic images. In fact, errors such as false image atoms, split peaks, and shifts in the peak position can be caused by these anisotropies. On the other hand, there is at least one beneficial effect of anisotropy in the scattering amplitude. A scattering amplitude that is sufficiently focused in the backscattering direction is actually able to greatly improve the achievable image resolution in the angular direction. This will be demonstrated in reference to the As/Si(100) system.

In our experiment, a Si(100) sample was heated at 1300 °C for 8 s, resulting in a clean, two-domain (2×1) diffraction pattern. An effusion cell was used to deposit ten monolayers (ML’s) of As on the surface. During this time, the sample was maintained at 380 °C, and the surface As coverage saturated at 1 ML. The sample was post-annealed for 120 s at the same temperature. Subsequent anneals at this temperature were seen to have no effect on the resulting diffraction pattern, nor on the line shape or intensity of the photoemission spectra of the As-3d and Si-2p core levels. This indicates that the As coverage remained unchanged by annealing at this temperature, after initial desorption of As coverages in excess of 1 ML.

Photoemission spectra were collected at the 1-GeV storage ring Aladdin at the Synchrotron Radiation Center (Stoughton, WI). A total of 31 emission directions were used in data collection, and for each direction 40 As-3d spectra were taken using a hemispherical analyzer with an angular acceptance of ±1.5°. The polar emission angles covered a range of 0<θ<70° relative to the surface normal. The azimuthal angles covered a range of 0<φ<45° relative to the [110] direction. The density of angles taken was higher in the solid angle region near the expected atomic locations. The data set was expanded using the fourfold rotation symmetry and appropriate mirror symmetry of the Si(001)-(2×1) surface. These symmetry operations expand the number of emission directions to 320, resulting in a total of 12 800 points in k space within the range of 3.4<k<6.3 Å⁻¹.

Figure 1 shows a schematic model of the surface structure to be compared with our experimental results. The As atoms form dimers in the top layer. Depending on the surface termination of the Si lattice, the dimer bond can take on two possible, mutually orthogonal orientations. Figure 1 represents just one of the two possible domain orientations. In the case shown, there are two As emitters in each unit cell, and each is bonded to two Si atoms in the layer below. Together, there are four first-neighbor Si atoms located at x = ±0.5 Å, y = ±1.9 Å, and z = −1.4 Å relative to the As
emitters. The other domain yields an identical set rotated by 90° about the z axis, and therefore a total of eight first-neighbor Si atoms are expected in the holographic images.

Atomic images were formed from the photoemission data using standard holographic techniques, including the use of the derivative method for intensity normalization to improve data accuracy.\(^\text{13}\) Figure 2 shows three mutually orthogonal planar slices of the holographic image across an expected atomic location. Figure 2(a) is a 6×6-Å slice at \(z = -1.4\) Å below the emitter. In this plane, we expect to see the atomic images of the eight first-neighbor Si atoms, and the experimental results are indeed just as expected. The locations of the atomic images are in excellent agreement with the expected positions marked by the crosses. The image consists of four pairs, and the two atoms within each pair, separated by a mere 1 Å, are well resolved. Rayleigh’s criterion for resolution requires that the saddle-point intensity between the image atoms be \(8/\pi^2 = 0.81\) times the intensity at the peak of the image atoms. In our image, the saddle point is at 0.45 of the peak intensity, clearly exceeding the Rayleigh’s criterion. A Gaussian fit of the atomic images yields a full width at half maximum (FWHM) of 0.72 Å in the direction connecting the two atoms in a pair. Figures 2(b) and (c) show 6×3.6-Å \(xz\)-planar slices at \(y = 1.9\) and 0.55 Å, respectively, with the origin of the planar coordinate system in each case indicated by a star. Again, the results are in good agreement with the expected atomic positions as indicated by the crosses. By symmetry in the \(xy\) plane, the three slices in Fig. 3 cut through each atomic image in three mutually orthogonal planes. The elongation of the atomic images in Figs. 2(a) and (c) along the radial direction is related to the finite range in \(k\) for the data set.

The \(xy\) in-plane resolution is significantly better than expected based on traditional simple models of photoelectron holography. In such models, the diffraction intensity modulation is ascribed to phase differences caused by path length differences, and variations in the electron scattering amplitude are taken to be a complicating factor that can lead to artifacts and image degradation. In the standard sweeping cone methods of holographic analysis, such as those introduced in Refs. 2 and 3, the angular integral of the Fourier-like holographic transform is limited to a cone centered about the backscattering direction. A small cone angle is desirable from the standpoint of limiting the phase variation resulting from electron scattering. However, too small a cone angle can lead to image broadening in accordance with the uncertainty principle. Typically, a cone angle \(\sim 60°\) (full angle) was chosen as a compromise in previous studies. This would not have allowed us to resolve the two atoms in a pair in the present case.

Paradoxically, the image shown in Fig. 2 was obtained instead with a very small analysis cone angle of 15°, which allowed us to achieve the sub-angstrom resolution. Clearly,
FIG. 3. Cuts at \( z = -1.4 \text{ Å} \) of holographic images for the As/Si(100) system using three different analysis cone angles indicated on top. (a)–(c) are simulated images assuming an isotropic electron scattering factor. (d)–(f) are experimental results. (g)–(i) are simulated images assuming a 35° angular spread of the backscattering maximum. The crosses indicate expected atomic locations and the white stars indicate the origin of the \( xy \) plane.

Image broadening according to the uncertainty principle cannot be the sole factor in determining the image resolution. Figures 3(a)–(c) illustrate this point. These are simulated holographic images for a cut at \( z = -1.4 \text{ Å} \), with an \( xy \) range chosen to show just the bottom pair of the eight first-neighbor Si atoms seen in Fig. 2. The simulation assumes an isotropic electron scattering amplitude and a constant phase (within the cone angle used for analysis), but otherwise the data structure is similar to the experimental set. An analysis cone angle of 15, 35, and 90° is used for Figs. 3(a)–(c), respectively. The two atoms are resolved only in Fig. 3(c), where a large 90° cone leads to a better defined atomic image in agreement with the uncertainty-principle argument.

Figures 3(d)–(f) are the corresponding images obtained with the same set of analysis cone angles on the real data. The 90° cone angle yields a smeared image that no longer shows atoms. This is because phase variations, conveniently ignored in the isotropic model, are important in the real data, and such phase variations are known to give rise to artifacts at large cone angles. The image becomes better at smaller cone angles, and at 15°, two well-resolved atoms are observed as in Fig. 2.

Figures 3(g)–(i) are simulated holographic images illustrating the important physics left out in the simplified models; namely, a strongly anisotropic electron scattering amplitude peaked in the backscattering direction can lead to better image definition. In this set of simulations, the electron scattering amplitude is assumed to be Gaussian-like with a 35° angular spread centered about the backscattering direction, which is a fairly good representation of the As/Si case as will be discussed below. As the analysis cone angle gets smaller, the image definition becomes better, and at an analysis cone angle of 15° [Fig. 3(g)], the two atoms become resolved as in the experiment. Physically, such strongly focused backscattering leads to a beam of electron emission in the direction connecting a Si scatterer to an As emitter. A large analysis cone [e.g., Fig. 3(i) at 90°] will pick up this emission over a wide angular range, leading to a blurred image. A small analysis cone, however, can pinpoint the direction of this focused emission, leading to a sharp image. This improved image definition does come at a price; namely, it is important to have sufficient data covering a dense set of angles, so that, upon broadening by the analysis cone angle, they form an overlapping set. A coarse set of data can easily miss the backscattering direction, resulting in no signal at all from the atom of interest.

The question, then, is if there is evidence that the backscattering amplitude is that narrowly focused. Partial wave phase shifts for scattering from Si (and other elements) can be obtained from a number of sources, for example, the NIST Elastic Electron Scattering Cross Section Data Base v. 2.0. This allows one to calculate the angle-dependent scattering amplitude, \( f(\theta) \). The result of this calculation at 100 eV, assuming a plane wave incident on Si, is shown in Fig. 4 as the dotted curve. This curve shows a broad maximum centered about the backscattering direction (\( \theta = 180° \)) with a FWHM of about 90°. This broad angle is not far from the isotropic approximations mentioned earlier.

We can take the correction a step farther. The assumption that the photoemitted electron impinges upon a Si scatterer at a distance of 2.4 Å away as a plane wave is a poor one. The curvature of the wave must be taken into account, and such curved-wave corrections have been discussed in the literature.20–22 As an estimate, the dashed curve in Fig. 4 is deduced from an experiment for a photoelectron from a Ga 3d core level scattering off of Si(111).
scattering maximum to an angular FWHM of about 45°. For the As/Si system under consideration, the initial core level is a 3d state, and the electron is excited into p and f waves. Although states with higher angular momenta have been discussed, the analysis is much more complicated, as the resulting correction depends on the emission direction, incident photon polarization, and relative atomic positions. The solid curve in Fig. 4 represents an experimentally determined scattering amplitude partly due to the curved nature of the photoelectron wave emanating from the emitter. The result is a directed beam of emission allowing a better geometrical definition of the image. This phenomenon appears to be quite general, and can be compared to the utility of the forward focusing effect often employed in x-ray photoelectron analysis of surface structure.11

In conclusion, holographic images of the As/Si(100) system have been presented, which are in excellent agreement with the expected atomic geometry. Sub-angstrom resolution has been achieved, allowing atoms separated by 1 Å to be resolved. Such resolution is significantly better than expected based on an uncertainty-principle analysis of the holographic transform. To achieve this resolution, an unusually small analysis cone angle must be used. The improvement in resolution can be attributed to a highly focused backscattering amplitude partly due to the curved nature of the photoelectron wave emanating from the emitter. The result is a directed beam of emission allowing a better geometrical definition of the image. This phenomenon appears to be quite general, and can be compared to the utility of the forward focusing effect often employed in x-ray photoelectron analysis of surface structure.11

This work was supported by the U.S. Department of Energy (Division of Materials Sciences, Office of Basic Energy Sciences) under Grant No. DEFG02-91ER45439. The Synchrotron Radiation Center of the University of Wisconsin-Madison is supported by the U.S. National Science Foundation Grant No. DMR-00-84402. An acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the U.S. National Science Foundation Grant Nos. DMR-99-75182 and DMR-99-75470 for partial personnel and equipment support in connection with the synchrotron beamline operation.

18 The Department of Energy “NTEAM” project.