Photoelectron holography of the In-terminated Si(001)-(4×3) surface

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Photoelectron holography is used to examine the structure of a complex surface, which has been debated in the literature. This is the (4×3) reconstruction of the In-terminated Si(001) surface. The seven models previously proposed for this system are presented, and the holographic atomic image resulting from experiment is used to identify the correct model.

For over a decade, the technique of photoelectron holography has been the subject of numerous studies involving theoretical, modeling, and experimental work in an effort to bring it to its fullest potential.[1–6] Unlike other diffraction techniques based on refinement of an assumed model, which may or may not be correct, this technique is capable of producing three-dimensional atomic images of surfaces by direct data inversion, and is thus free from such modeling errors. Another advantage is elemental specificity, allowing one to examine distinct chemical sites. The resulting holographic image consists of atoms neighboring an emitter site whose core level is measured by photoemission. While this technique has been demonstrated to work for simple model systems, it has remained a challenge for practical applications involving more complicated surfaces where such direct methods would be most useful. The difficulty lies in the fact that the number of possible atomic sites neighboring an emitter increases rapidly as the complexity of the surface structure increases. With a finite achievable resolution, the numerous atomic images can merge, diminishing the information content. Over the past several years, significant progress has been made in the holographic method that allows optimum use of data to achieve a predictable resolution. The present work takes advantage of the latest developments to solve the structure of a complex surface, the In-terminated Si(001) surface with a (4×3) reconstruction. This surface has been studied with various other techniques, each of which provides valuable information, but none can completely specify the structure with certainty. As many as seven models have been proposed previously. Only one of these agrees with our holographic image, and this is identified as the correct structure.

A summary of the seven models is given below, and the large differences among these models illustrate the potential pitfalls in using indirect information for model construction. This system was studied in 1991 by Baski, Nogami, and Quate[7] using scanning tunneling microscopy (STM). They were unable to achieve atomic resolution of the In adatoms, but were able to define certain limits for proposed models of the unit cell. In 1994, Steele et al.[8] studied this system using impact-collision ion-scattering spectrometry (ICISS) and STM. Based on the STM work, they proposed four possible models for the unit cell. They then compared these models with ICISS data and determined a closest match with that

data from their models. In 1996, Yeom et al.[9] examined this same system with core-level photoemission spectroscopy and determined that only one component could be resolved for the In 4d core level, thus suggesting that the In adatoms should all lie in nearly identical bonding sites. This contradicted the models proposed by Steele et al.

Zotov et al.[10] used a low-energy electron-diffraction technique, along with Auger electron spectroscopy, in 1997, to demonstrate that when H atoms were used to replace the In atoms in this system, a (4×1) reconstruction remained in the Si substrate.[11] This should be taken into account in a successful model of this system. They later[12] proposed a model which would satisfy this requirement, as well as requirements of previous studies. At around the same time (1998), a study by Bunk et al.[13] using surface x-ray diffraction determined a structure for this system that also satisfied the "nearly identical sites" requirement of Yeom et al. The original study by Bunk et al. didn't consider the structure proposed by Zotov et al. for comparison to their x-ray-diffraction results. In a later comment on Zotov et al.'s article, Bunk et al.[14] reported on their effort to fit the structure proposed by Zotov et al. with their x-ray-diffraction data. They concluded that fits to that model were inadequate when compared to their own model. Shortly thereafter, as a result of using a macroscopic counting technique with STM to analyze the number of In atoms in each unit cell, Saranin et al.[15] modified the previously proposed model of Zotov et al. to include one In adatom in addition to the six replacement atoms of the previous model, for a total of seven In atoms per (4×3) unit cell. This also brought the total number of proposed models for the system up to seven. These seven models are presented in Fig. 1. In each case, two (4×3) unit cells are shown in both top and front views. For the top view, the 3× reconstruction direction is along the vertical.

Photoelectron holography, with its element-specific, direct imaging capability, would be useful for resolving this case. Our work is a holographic study based on the In 4d core-level emission, which should yield images of the Si neighboring atoms. However, considering that the reconstruction involves approximately six or seven different In atoms in the unit cell in various local bonding geometries, the holographic images, reflecting a superposition of these geometries, can be fairly complicated. Because the rectangular (4×3) unit cell has a lower symmetry than the (1×1) unreconstructed Si
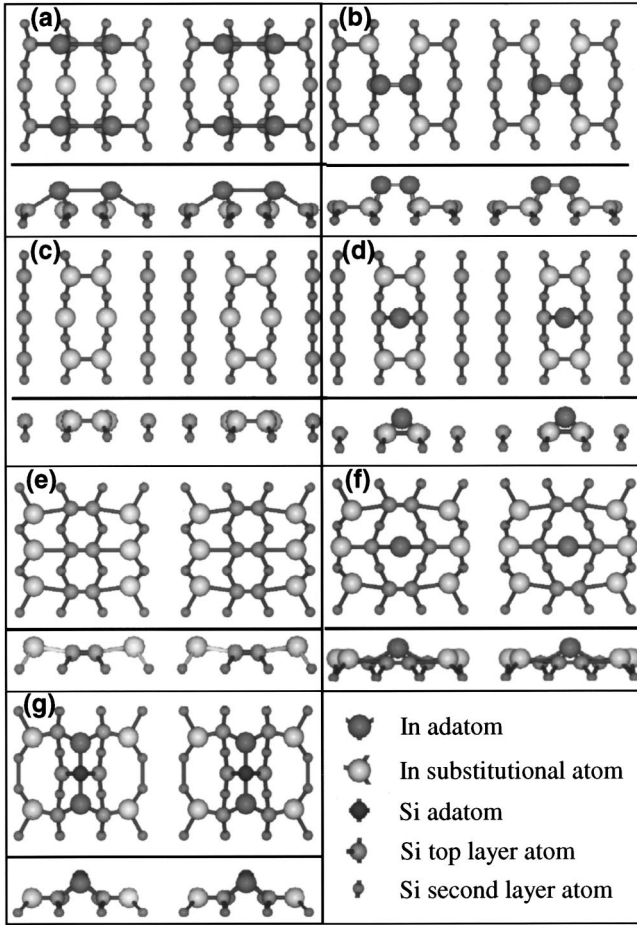
FIG. 1. Proposed models for In/Si(001)-(4×3). (a)–(d) represent Steele *et al.*'s models. (e) represents the model from Zotov *et al.* Saranin *et al.*'s model with seven In atoms per unit cell is shown in (f). (g) is the model presented by Bunk *et al.* Both top and side views are presented for each model. The [110] direction is to the right.

substrate, two orthogonal domain orientations can be simultaneously present for commonly used Si substrates. This results in a superposition of holographic images from these two domains and effectively doubles the number of imaged atoms. This causes additional complication, and must be avoided if possible. The two-domain problem is solved in our experiment by using a vicinal substrate with a miscut of about 4° towards the [110] direction. A miscut of this size is known to favor double steps on the Si(001) surface instead of the usual single steps. After In deposition, a single-domain orientation of the (4×3) reconstruction was obtained,[16] as verified by reflection high-energy electron diffraction in our experiment.

Our preparation of the (4×3) reconstruction of the In-terminated Si(001) surface followed the recipes given in the literature, and involved deposition of about three monolayers of In at elevated temperatures followed by prolonged annealing to desorb the excess In. Photoemission spectra of the In $4d$ core level were collected at the 1-GeV storage ring Aladdin at the Synchrotron Radiation Center (Stoughton, Wisconsin). A total of 46 emission directions were used in data

collection, and for each direction 40 spectra were taken using a hemispherical analyzer with an angular acceptance of ±1.5°. The polar emission angles covered a range of 0° < θ < 65° relative to the surface normal. The azimuthal angles covered a range of 0° < φ < 90° relative to the [110] direction. The data set was expanded using the twofold rotation symmetry and appropriate mirror symmetry of the surface. These symmetry operations expanded the number of emission directions to 184, resulting in a total of 7360 points in k space within the range of 2.3 Å^{-1} < k < 5.5 Å^{-1}.

Holographic images were derived from the acquired intensity data using the derivative method in order to minimize experimental errors caused by drift and variation in experimental parameters, and a sweeping-cone algorithm was employed to overcome the phase problem.[4–6] A brief outline of the method follows. Along each emission direction $\hat{\mathbf{k}}$, the measured logarithmic intensity derivatives are numerically integrated to yield the intensity $I(k,\hat{\mathbf{k}})$ as a function of photoelectron wave vector k. This is then subtracted by and normalized to a smooth background function $I^0(k,\hat{\mathbf{k}})$ to yield the fine-structure function

$$\chi(k,\hat{\mathbf{k}}) = \frac{I(k,\hat{\mathbf{k}}) - I^0(k,\hat{\mathbf{k}})}{I^0(k,\hat{\mathbf{k}})},$$

which shows oscillations caused by interference from scattering by near neighbors. The holographic transform involves a three-dimensional numerical integration in the reciprocal space using all of the fine-structure functions deduced from the experiment, and is given by

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

where $g(\mathbf{k})$ is a window function that incorporates a sweeping angular cone and a Welch function in k matched to the experimental data range. A calculated backscattering phase shift ϕ is employed, but its effect is negligible for the present system because it is fairly constant over the range of the experiment.[6]

We define the coordinate system with the In adatom at the origin, the x and y directions along [110] and [$\bar{1}$10], respectively, and z along the surface normal. Figure 2(h) shows an experimental image corresponding to an xy planar cut at $z = -1.4$ Å. This z value corresponds approximately to the majority of expected first-neighbor Si atoms, and shows more details than cuts at other heights. The image has a size of 6 Å×6 Å, and is centered about the origin. The results show four bright peaks at $y = \pm 1.4$ Å and $x = \pm 0.4$ Å. In addition, a "tail" can be seen extending from these peaks around toward the x axis, together with some weaker features.

Figure 2 also contains holographic images calculated from the seven models discussed above, using parameters and data structure corresponding to the experiment. These are essentially (fuzzy) ball models involving a superposition of neighboring atoms for all inequivalent In emitters. Figures 2(a)–2(g) are derived from the models presented in Figs.
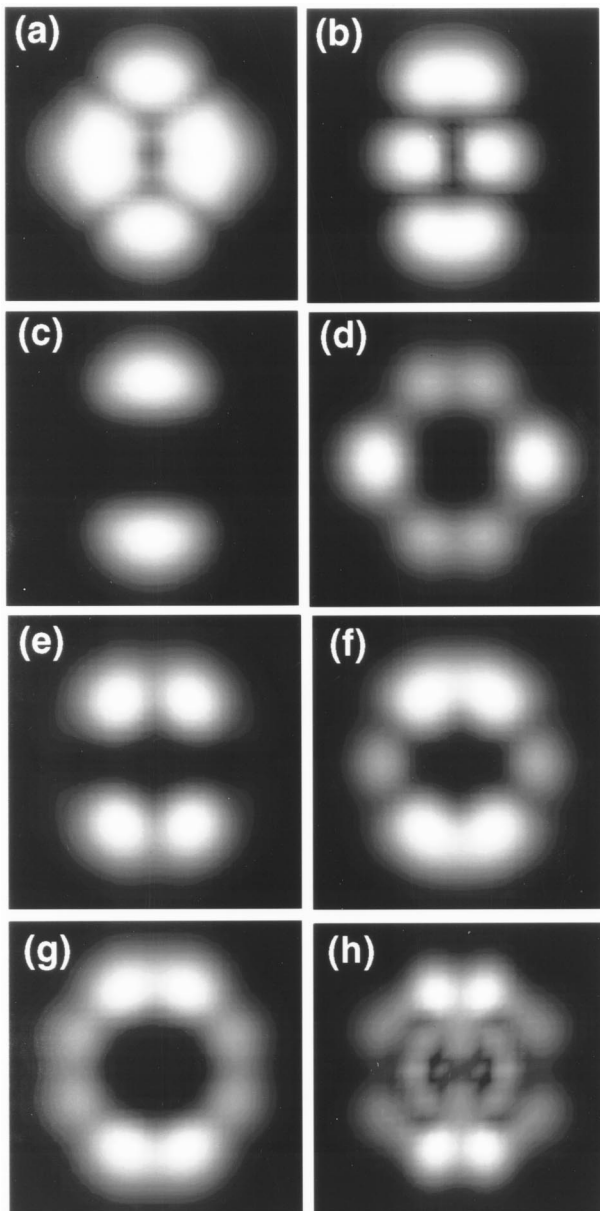
FIG. 2. Planar cuts of holographic images at $z = -1.4$ Å. (a)–(g) are calculated holographic images derived from the seven proposed models shown in Figs. 1(a)–1(g), respectively. (h) is the experimentally determined holographic image. The [110] direction is to the right. All images have the same scale of 6 Å × 6 Å.

axis, but no sign of the "tail" from the experimental result. Figure 2(f) has a "tail" that is somewhat similar to the experimental data, but this "tail" has its intensity peaked at the x axis, whereas the experimental result shows a node in the tail at the x axis. Figure 2(g) contains both the two bright atomic pair images and a "tail" that dies off near zero at the x axis. Thus, the major features of the experimental results are only reproduced by the model shown in Fig. 1(g). In this model, the tail in the image arises from atoms 0.4 Å above the image plane.

The experimental image additionally contains some weak features near the center of the picture, which are not reproduced by any of the models. The likely source for this discrepancy is the high density of step edges on the surface. The 4° miscut is necessary in the present experiment to suppress two-domain formation, but leads to a relatively small plateau width of about 40 Å. The result is that some 20% of the unit cells can be expected to be partially distorted or modified by the step edges. Such "misplaced" indium atoms must be expected to add some weak features to the primary image.

Although the present study is a success, it illustrates the limitations of photoelectron holography as a method of direct imaging for complex surfaces. Namely, numerous neighboring atoms in the image involving inequivalent sites can merge, making it impractical to reconstruct the atomic structure directly from the data. In the present case, we have employed a hybrid method that is somewhere in between traditional diffraction analysis and true holographic reconstruction. A comparison of the experiment and model is carried out in real space to identify the correct structure. This is still better than pure diffraction methods where the comparison is made in reciprocal space; very different real-space models could yield similar diffraction results, thus possibly leading to erroneous conclusions.

To summarize, this work is an effort to use photoelectron holography to solve the structure of a complex system. Our photoelectron holographic image for In on Si shows that the model developed by Bunk *et al.* based on x-ray diffraction is the correct model. This work establishes photoelectron holography as a practical structural tool even for complex systems.

1(a)–1(g), respectively. Comparing the models to the experimental result, we note that Figs. 2(a), 2(b), and 2(d) show bright images along the x axis that are clearly missing in the experimental result. Figure 2(c) has no such image, but the large intensity maxima centered about the y axis clearly do not correspond to the experimental result. Figure 2(e) does have the two bright atomic pair images centered about the y

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