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Experimental surface charge density of the Si (100)-2×1H surface

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We report a three-dimensional charge density refinement from x-ray diffraction intensities of the Si (100) 2×1H surface. By paying careful attention to parameterizing the bulk Si bonding, we are able to locate the hydrogen atoms at the surface, which could not be done previously. In addition, we are able to partially refine the local charge density at the surface. We find experimentally an increased, slightly localized bond density of approximately 0.31 electrons between each Si atom pair at the surface. Both the atomic positions and the charge density are in remarkably good agreement with density-functional theory calculations.

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The subject of surfaces has been the epicenter of numerous studies in recent years, particularly with respect to applications in catalysis, thin films, and self-assembly of nanostructures where the surface-to-volume ratio is particularly large. The thrust of these scientific explorations has been the use of both theoretical and experimental methods to probe surface chemical and electrical properties. However, if the electron charge density at the surface is known, at least in principle, many of these properties can be calculated as functionals without need for further experimentation.[1]

For many years, the implicit assumption made in determining atomic positions from x-ray diffraction (XRD) data was that all electrons are present around atomic nuclei in rotationally averaged (*s*-type) ground states. It was first theorized by Debye in 1915 that x-ray diffraction could be used to directly measure charge densities in solids,[2] but experimental errors were far too large for the sparse densities of interatomic electrons to be localized. Today, the widespread use of synchrotron radiation has brought about a substantial reduction in experimental errors, which has enabled several groups to measure charge densities for both bulk extended solids,[3–6] and large organic molecules (see Refs. 7–9 for a thorough review of x-ray charge density studies). However, the experimental determination of charge densities on *surfaces* presents much larger challenges due to the inherently larger errors and to date has been largely neglected by the x-ray community in favor of bulk studies. To the best of the authors' knowledge, there is only one publication of experimental charge density measurements at a surface,[10] which utilized transmission electron diffraction to reveal increased covalency at the MgO(111) surface.

In this note we report a three-dimensional charge density refinement from x-ray diffraction intensities of the Si (100) 2×1H surface. By paying careful attention to modeling the bulk Si bonding, we are able to locate the hydrogen atoms at the surface, which could not be done previously. In addition, we are able to partially refine the local charge density at the surface. We find, experimentally, a bond density of approximately 0.31 electrons between each Si atom pair at the surface. Both the atomic positions and the charge density are in remarkably good agreement with density-functional theory (DFT) calculations.

The Si (100)-H surface has been well studied both experimentally and computationally and is a model system for gas adsorption on semiconductor surfaces. Most recent studies have utilized scanning tunneling microscopy to probe the periodicity and hydrogen occupancy of the 1×1, 2×1, and 3×1 reconstructions as well as DFT calculations to determine the bond energies.[11–20] Although it is possible with these techniques to determine at which sites the hydrogen atoms reside, their precise three-dimensional location and the charge redistribution due to bonding have only been calculated. The XRD intensities from the 2×1H reconstruction have been carefully measured previously[21] but it was not possible at that time to stably refine the positions of the hydrogen atoms by using standard form factors from spherical Si atoms. As shown below, hydrogen can only be located by using more correct (nonspherical) electron densities for the Si bulk, since the charge density around the hydrogen atoms is of the same order magnitude as the nonspherical portion of the Si electron density.

Fitting the charge density at a surface is not as simple as fitting atomic positions in the bulk. In terms of fitting experimental diffraction intensities, the largest contribution comes from neutral-atom scattering, the zero-order approximation. We will define the first-order correction as the change in electron density on creating a bulklike bonding configuration, and the second-order correction as the distortions from the bulk bonding configuration by changes of bond lengths (and in principle, angles). A third-order correction would include surface-specific changes to the electron density. Our experience is that starting from the zero-order neutral-atom approximation it is very difficult (if not impossible) to obtain reliable results for a surface—therefore, our approach is to start from a density which already models well the bulk contributions so the smaller surface-specific effects can be isolated. Previous work on the MgO (111) surface used an initial first-order model,[10] here we will start from a second-order model.

To establish the second-order model, bulk charge densities were generated from extensive DFT calculations of bulk

Si using the WIEN2K code.[22] A 33-parameter model was fitted to 106 sets of theoretical structure factors (a total of 93 142 data points) computed from valence charge densities that included bulk Si with (1) a range of lattice parameters from 4.892 to 7.609 Å; (2) bulk Si with small variations of bond angles; and (3) four (artificial) larger supercells. The full method and model is described elsewhere.[23] The final model used a pair of Gaussian excess features centered between each Si-Si pair (bond-centered pseudoatoms) as well as a Gaussian depletion region opposite the bond. The magnitude, position, and width of these features can be simply parameterized in terms of the silicon-silicon bond length, ignoring bond-angle dependencies. In the second-order model, the total density for each silicon atom (at the origin for simplicity) can be written as

$$\begin{aligned}\rho_a(\vec{r}) = \rho_{core}(\vec{r}) + \rho_{valence}(\vec{r}) \\ + C_e\{(\pi/W_+)^{3/2}\exp(-\pi^2|\vec{r}-\vec{r}_+|^2/W_+) \\ - (\pi/W_-)^{3/2}\exp(-\pi^2|\vec{r}-\vec{r}_-|^2/W_-)\},\end{aligned} \tag{1}$$

where ρ is the charge density, C_e is the marnitude of the charge of the bond-centered pseudoatom Gaussians, W is the Gaussian width, and $r_{+,-}$ are the pseudoatom positions in the bond and antibond directions. In this model, C, W, and $r_{+,-}$ are closed functions of the Si-Si bond length.

In this model, ρ_{core} represents the 1*s*, 2*s*, and 2*p* states and is computed from an atomic orbital expansion,[24] and ρ_{valance} was determined by fitting the 3*s* and 3*p* valence states to the aforementioned 93 142-point DFT dataset using a nine-term Slater-type orbital expansion.[23] The difference between the the second-order charge density and the atomic orbital expansion of Su and Coppens[24] in the plane of the Si-Si bond is shown in Fig. 1. Because of the parameterization, the refinement of atomic positions directly refines the electron charge density because Eq. (1) is a closed function of the Si-Si bond length; therefore, the use of the second-order model does not contribute any additional adjustable parameters to the experimental fit.

The experimental XRD data used was obtained from Ref. 21 and collected at the wiggler beamline BW2 of the second generation synchrotron radiation facility HASYLAB in Hamburg, Germany. The atomic positions, anisotropic temperature factors for only the top Si pair, and bulk temperature factors for Si and H were refined using a robust reduced χ figure of merit,

$$\chi = \frac{\sqrt{2}}{N-P}\sum_{hkl}\frac{|I_{hkl,calc} - sI_{hkl,obs}|}{\sigma_{hkl}}, \tag{2}$$

where N is the total number of data points (130), P is the number of fitted parameters [N-P is the number of "degrees of freedom" (DOF)], I_{hkl} are measured intensities, s is a scaling term, and σ_{hkl} is the total corresponding error for each reciprocal lattice vector. The scaling term was calculated from a confidence scaled intensity conservation condition

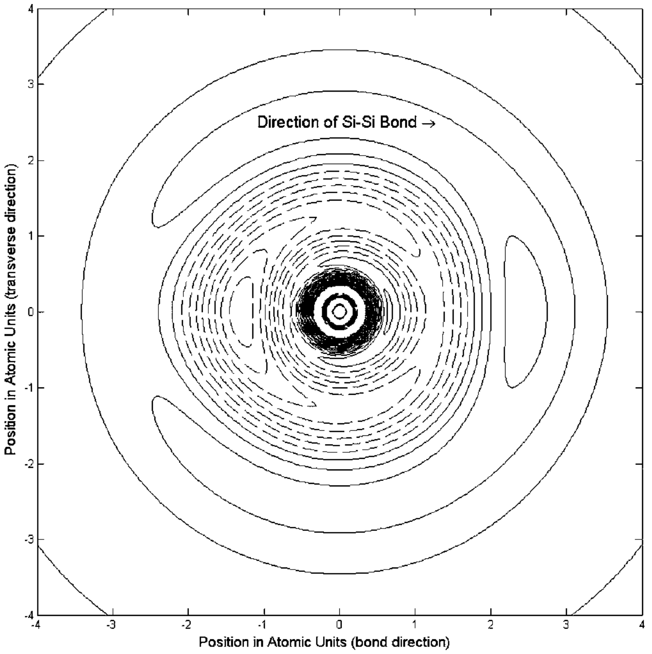

FIG. 1. Charge density difference between the second-order model and the conventional atomic orbital expansion of Ref. 24 in the plane of the Si-Si bond (dashed lines negative, contour interval: 0.01 $e^-/\text{Å}^3$). Reproduced from Ref. 23 with permission from IUCr (http://journals.iucr.org/).

$$s = \frac{\sum I_{calc}{}^2/\sigma}{\sum I_{obs}I_{calc}/\sigma}, \tag{3}$$

to ensure that the χ fit also produced a good $R1$ value. The hydrogen atoms were treated as neutral atoms without bonding considerations, and a boundary condition of bulk bond lengths was imposed from the seventh layer of the slab for all fits performed.

To determine the statistical validity of including hydrogen in either the neutral atom or second-order model, the Hamilton R-test[25] was used. As we used a robust χ fit rather than χ^2 as presented in Hamilton (1965),[25] the form of the "weighted R factor" must be modified to

$$R'' = \frac{\sum |I_{calc} - I_{obs}|/\sigma}{\sum I_{obs}/\sigma}. \tag{4}$$

Using the zero-order neutral Si atoms, the best fit had a χ of 1.314 ($R''=0.1047$). (Table I summarizes all the models tested.) However, it was not possible to uniquely define the position of the hydrogen atoms because their isotropic temperature factors were always unphysically large ($B > 100$ Å^2), and they were often expelled from the surface with unrealistic refined bond lengths of over 5 Å. With neutral atoms, a comparable fit to the experimental data could be obtained by completely removing the hydrogen atoms, $R''=0.1046$ in this case. The addition of hydrogen atoms adds three adjustable parameters, x position, z position, isotropic B, to the nonhydrogen model having DOF=108. The Hamilton R test shows that the improvement due to the addition of

TABLE I. Summary of fitting results.

Model order	Hydrogen Constraint	χ	R''	DOF	DOF$^*\chi$	Confidence Level
Zero	Free	1.314	0.1046	106	139.2	N/A
Zero	Fixed	1.290	0.1057	109	140.6	0.0%
Zero	No H	1.277	0.1047	109	139.2	0.2%
Second	Free	1.261	0.0995	105	132.4	86%
Second	Fixed	1.270	0.1031	108	137.1	0.0%
Second	No H	1.257	0.1021	108	135.8	N/A

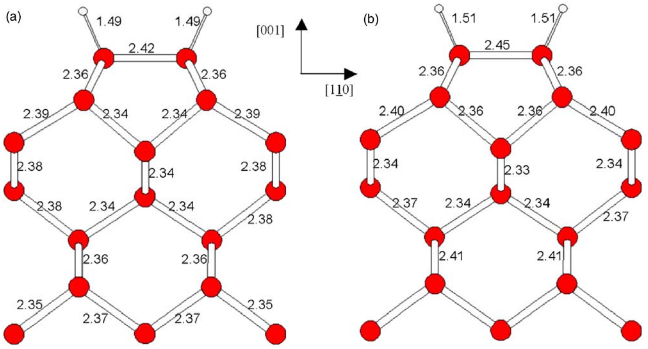

FIG. 2. (Color online) Si-Si bond lengths in Å projected onto (110) plane. (a) calculated; (b) experimental (second-order model).

hydrogen in this case is not reliable (it is at a 0.2% confidence level). The zero-order model does not give a tenable result unless one adds chemical constraints to fix the hydrogens to be at "reasonable" locations. However, this yields $R''=0.1057$, larger than removing the hydrogen, so is not justifiable and statistically is at a 0% confidence level.

Using the second-order model yielded a refined χ of 1.261 ($R''=0.0995$) which is 4.2% lower than the neutral case. While small, the improvement is statistically significant; the probability of such an improvement due to random chance is $\exp(\text{-DOF}^*\Delta\chi)=0.001$. This improvement indicates that the second-order model charge density is indeed more correct than the conventional neutral atom model. The Hamilton test cannot be used to compare two fundamentally different models, but we can analyze the significance of the hydrogen atoms in the second-order model. Removing the hydrogen atoms slightly reduced χ to a value of 1.257, but of much greater significance, the weighted Hamilton R factor increased to $R''=0.1021$. This increase in R'' indicates that the inclusion of hydrogen at the surface is valid at the 86% confidence level according to the Hamilton R test. This sugguests that only with the second-order model can one determine if the hydrogen atoms exist at all. Of particular importance, there was no need to add chemical constraints to fix the atomic positions of the hydrogens; with the second-order model both the positions and temperature factors refined stably to very reasonable values. Only this model where the near-surface charge density is allowed to vary gave results which are physically and/or chemically reasonable.

To further test whether or not the results obtained from the second-order model were reasonable, we performed a separate set of DFT calculations using the WIEN2K code[22] (a full-potential all-electron code based on the use of linearized augmented plane-wave+local-orbital [APW+lo] basis sets). We used a seven-layer slab of the surface with an inversion center and 12 Å of vacuum between surfaces. The resolution of the calculation was determined by the maximum angular momentum for the radial wave functions ($l_{\max}$) of 10, muffin-tin radii (RMT's) of 1.65 for Si and 1.10 for H, an RKMAX (the smallest RMT* reciprocal space limit) of 4.5, and a k-point mesh of $6\times3\times1$. The structure was relaxed until all forces acting on the atoms were less than 4 m Ry/a.u.

After rescaling to correct the difference between the real and DFT calculated lattice parameters, the DFT calculated Si-Si bond lengths differ from earlier neutral atom refinements[21] by a root mean square 0.049 Å, and by 0.029 Å from the second-order model described above, both of which are shown in Fig. 2. This further supports the fundamental improvement of the second-order model: when the valance charge density is incorrect, even the atomic cores will not refine properly. All experimental Si-Si bond lengths have an error of 0.01 Å, with the exception of the bottom Si pair (and the bulk-constrained bottom interface layers) which have an error of 0.04 Å (an artifact of the bulk bonding condition imposed in the x-ray refinements, true for both the zero- and second-order fits).

The DFT-calculated Si-H bond length (core-to-core) was 1.49 Å which is in agreement with previous studies,[26] and within the standard error of the experimental value of 1.51(±0.1) Å. The position of the H atom refined from the experimental data was quite localized as indicated by a temperature factor B of 6.2 Å^2 (equivalent to a positional uncertainty of 0.1 Å). Although this temperature factor is large in absolute terms, its effect is small because the temperature-independent component of the hydrogen scattering factors is a strongly decaying function of the scattering vector s, and is quite favorable to the $B>100$ Å^2 obtained when the second-order fit is not used.

The agreement between the DFT calculated valence charge densities [Fig. 3(a)] and the experimentally determined ones is remarkably good. Figures 3(a) and 3(b) show the charge difference map with respect to neutral Si atoms by summing the charge in the plane of the unit cell where the atoms reside (i.e., summing along [110]), for both the theoretical and experimental analyses, respectively. There is a region between each atom pair in the plane with an excess of electrons (solid lines). To maintain neutrality with respect to each individual Si, a depletion region (dashed) is seen opposite the bond. In the DFT calculations, the integrated size of the excess regions is approximately 0.37 e^- and the depletion regions are approximately -0.35 e^- in occupancy; both figures ±0.03 e^- depending upon the bounds of the integral. There is some leakage of the hydrogen charge to the top Si atoms which is redistributed to its bonding regions, making their density slightly larger, but the hydrogen atom retains a charge of 0.97 e^- as determined by numerical integration of the projection. The charge density near the surface Si-Si dimer appears very bulklike and the charge from the hydrogen atoms is quite localized.

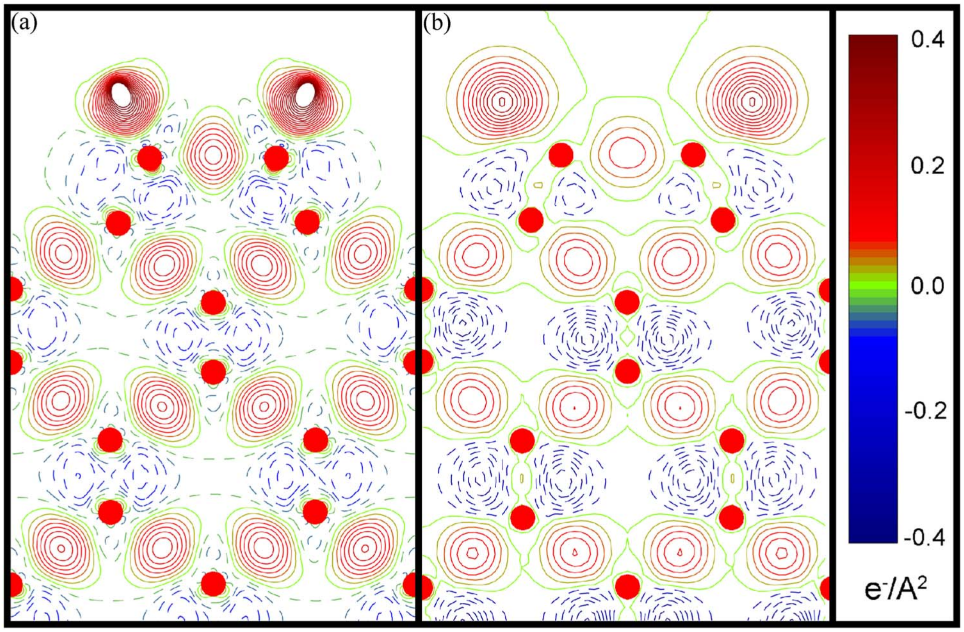

FIG. 3. (Color online) Charge difference maps with contours in intervals of 0.025 $e^-/\text{Å}^2$ (dashed lines negative) projected onto a (110) plane; (a) DFT, calculated; (b) experimentally refined from second-order model.

The experimental charge density refined using the second-order model [Fig. 3(b)] is very similar to the DFT results discussed above. (For reference, the figure shows the charge density difference for the fully refined bonding model minus a neutral-Si model with the same atomic coordinates and temperature factors.) Because the resolution of the experimentally determined charge density was limited to 0.25 Å (compared to 0.04 Å for the calculations), some discrepancies in graphical representation are expected. In the experimental fit, the bulk midbond excess features and external depletions have charges of ±0.31 e^-, respectively. It is important to note that the bonding charge from the experimental data for the top Si atoms is on the same order as that in the bulk indicating a Si-Si single bond as expected when hydrogen terminated and predicted from the DFT results. The midbond electron clouds refined from the experimental-data are slightly more delocalized than the DFT calculations suggest, which is reasonable because the experiments were carried out at 300 K rather than the 0 K DFT calculations. The hydrogen atoms are well localized, paralleling the DFT prediction. The hydrogen atoms also clearly exhibit more spreading in the lateral direction compared to the bond direction, which is expected at the surface since a single bond is more resistent to stretching than to bending.

In this paper we have presented the experimental three-dimensional determination of the surface charge density utilizing XRD and also report the evidence of directly measured surface hydrogen atoms on the Si (100)-2×1H surface. The localization of the hydrogen atoms was not possible without a model going beyond spherical, neutral Si atoms, and that accounts for charge transfer effects due to Si-Si bonds. Further exploration of surface charge density could in the future be achieved by collecting highly accurate, more extensive data sets, in particular in the direction normal to the surface, at shorter x-ray wavelengths at high-brilliance third generation sources. Although Si (001)-2x1H was used as a model system for this study, this technique may be used to investigate myriad other systems including organic molecules on Si for chemical-sensing and molecular-electronics applications with particular interest in the Si-C bond, nanoislands on catalytic surfaces, and superconducting thin films.

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