Reflectance Difference Spectroscopy: Experiment and Theory for the Model System Si(001):As and Application to Si(001)

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Reflectance difference spectroscopy (RDS), scanning tunneling microscopy, and calculations of the RDS spectra have been performed for the bare Si(001) surface and Si(001):As, thereby relating identified structures with RDS features. For the As-terminated surface, which exhibits a 2×1 symmetric As-As dimer structure, we demonstrate excellent agreement between measured and calculated spectra. For clean Si(001), which shows a more complex structure arising from dimer asymmetry, we provide identification of RDS spectral features arising from transitions between dangling-bond surface states.

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Reflectance difference spectroscopy (RDS), also referred to as reflectance anisotropy spectroscopy, is a powerful tool for characterizing the surfaces of crystalline materials [1]. Polarized light normally incident on a sample which has an azimuthally isotropic bulk optical susceptibility produces no difference in reflectivity as a function of azimuthal polarization angle. The surface, however, usually has a lower symmetry than the bulk and can lead to optical anisotropy. This can be probed by modulating the angle of polarization relative to the optical eigenaxes. Thus, for example, if the surface symmetry reduces from fourfold to twofold, then taking the difference between the reflectance for light polarized parallel and perpendicular to the surface axes provides a signal related only to the surface-induced electronic structure. Because light has a far smaller cross section for interaction with matter than many other probe beams, such as electrons, the RDS technique can also be applied to systems immersed in gas or liquid ambients.

RDS has been applied to various semiconductor surfaces [2,3]. What is still lacking, though, is a connection between the observed features in RDS spectra and the causative transitions. To provide such connections two additions to the RDS experiments need to be provided. First, one needs to characterize the (preferably simple) surfaces using independent means so that one is confident about what is being probed; second, one must perform theoretical calculations which can accurately delineate the contributions to the optical transitions at a particular energy.

In this Letter we report results of RDS, scanning tunneling microscopy (STM), and theoretical calculations of the RDS spectra for the As-terminated Si(001) surface and the clean Si(001) surface. Si(001)-(1×2):As exhibits a stable and well-understood atomic structure, and may therefore serve as a model system for assessing the accuracy of calculations of RDS spectra. Its small 1×2 unit cell facilitates theoretical calculations of the reflectance anisotropy. For this system we have obtained good agree-

ment between theory and experiment. In our investigations of the clean Si(001) surface we demonstrate that the dangling-bond surface states on the Si-Si dimers make a significant contribution to the RDS spectrum, and that the RDS spectrum is sensitive to the ordering of the dimers. Therefore, the disordered nature of the dimer buckling at room temperature could lead to complications in interpreting the spectra. Nevertheless, we have obtained reasonable agreement between experiment and calculations which employ 2×2 or 2×1 unit cells containing buckled Si-Si dimers.

All results described in this Letter were obtained on Si(001) samples rotated either 4° or 2.5° from (001) about a (110) axis. The clean Si samples, after annealing to 1030 °C, had predominantly two-atom high steps separating terraces of (2×1) reconstructed dimers. As seen for the 4° vicinal surface in Fig. 2(a), the dimerization direction was mainly parallel to the step edges. The surface optical eigenaxes are parallel and perpendicular to the dimerization direction. RDS sums the responses over the probe region. Therefore, equal areas of (2×1) and (1×2) domains cancel their local contributions to the resultant RDS signal. The vicinal surfaces allow us to order the dimers and thus maximize the contributions of the dimers to the RDS. A minor contribution might be expected to arise directly from the steps; however, we argue below based on the data that RDS features related to steps are insignificant relative to the net dimer response.

The RDS spectrometer was attached to a strain free window port having a line of sight normal to the sample on its holder in our research molecular beam epitaxy (MBE) system. (See Ref. [4] for further description of the MBE.) Samples were moved *in vacuo* between interconnected pods of the MBE and surface analysis system. One pod houses the STM. The temperature stabilized RDS system used a xenon arc lamp (for $h\nu = 2-5$ eV) and a quartz tungsten halogen lamp (for $h\nu = 1-3$ eV), spherical reflecting optics, MgF$_2$ Rochon polarizers, a quartz photoelastic polarization modulator, a

1/4 m grating monochromator, and a 76 channel linear diode array for multiplexed sensing of the wavelength dispersed, dc-normalized, ac signal.

The reflectance difference signal is $\Delta r/r = \mathrm{Re}[(2(\tilde{r}_{\bar{1}10} - \tilde{r}_{110})/(\tilde{r}_{\bar{1}10} + \tilde{r}_{110})]$, where $\tilde{r}_{\bar{1}10}$ and $\tilde{r}_{110}$ are the complex reflectivities for light polarized, respectively, perpendicular and parallel to the tilt axis direction. A well-defined rotation of the plane of polarization by a small angle δ is used to calibrate the spectrometer according to $\Delta r/r = 2\delta$. The RD spectra were taken at room temperature (RT). For each run two spectra were taken, corresponding to the sample [110] axis at $\pm 45°$ relative to the unmodulated polarization axis. The 90° phase shift produces an RDS inversion for sample-derived signals; however, systematic (small) baseline offsets do not change. Therefore, half the difference between spectra was taken for the final data to eliminate any such artifacts.

The calculation of the reflection anisotropy spectra was performed in a single-particle approximation which relates $\Delta r/r$ to electronic transitions between occupied and empty states of a thin slab of material. Following Manghi et al. [5] we calculate

$$\frac{\Delta r}{r} = \frac{8\pi d}{\lambda} \, \mathrm{Im}\!\left[\left(\frac{4\pi[\alpha_{xx}(\omega) - \alpha_{yy}(\omega)]}{\epsilon_b(\omega) - 1}\right)\right]. \quad (1)$$

In this expression $\epsilon_b(\omega)$ is the bulk dielectric function of Si, and $\alpha_{xx}(\omega)$ and $\alpha_{yy}(\omega)$ are components of the optical polarizability tensor calculated for a 16 layer centrosymmetric film of Si having a thickness of $2d \sim 40a_B$. Excitonic effects are beyond the scope of this work and are neglected. The optical response for light polarized along the dimers $\alpha_{xx}(\omega)$ will in general be different from that for light polarized perpendicular to the dimers $\alpha_{yy}(\omega)$. The real part of $\alpha(\omega)$ is obtained from the imaginary part by a Kramers-Kronig transformation.

Within the single-particle approximation, the band structure entering the calculation of the imaginary part of $\alpha(\omega)$ should be obtained from quasiparticle calculations [6]. Indeed, we have performed quasiparticle (QP) calculations for both the clean Si(001) surface [7] and the As-terminated surface [8]. In these and previous calculations [9] it has been found that the QP band structure is related to the LDA (local density approximation) band structure by a nearly rigid shift of the electron states relative to the hole states. Because it is impractical to calculate quasiparticle energies for each of the large number of electronic states required in the calculation of the dielectric functions, we have employed LDA band structures, but with the energy band gaps between occupied and empty states increased by 0.5 eV. For the calculation of the dielectric function we include all conduction bands within 1 Ry of the conduction band minimum for each of 128 k points on a uniform grid in the 2×1 irreducible Brillouin zone. For the 2×2 cells we employ an equivalent k point set consisting of 64 points. The LDA band structure is obtained from first-

principles pseudopotential calculations with a plane wave cutoff of 12 Ry for the As-terminated Si(001) surface and 10 Ry for the clean Si(001) surfaces [7].

In Fig. 1(a) we show an STM filled state image for a clean Si(001)-(2 × 1) sample passivated with a monolayer (ML) of As. The sample was prepared by saturating the sample surface at room temperature in an As_4 flux and then ramping the sample to 600 °C before turning the arsenic flux off. The dimerization axis is rotated by the addition of 1 ML, and the (1 × 2) to (2 × 1) ratio is typically 9:1. (The trenches running perpendicular to the steps are phase boundaries which
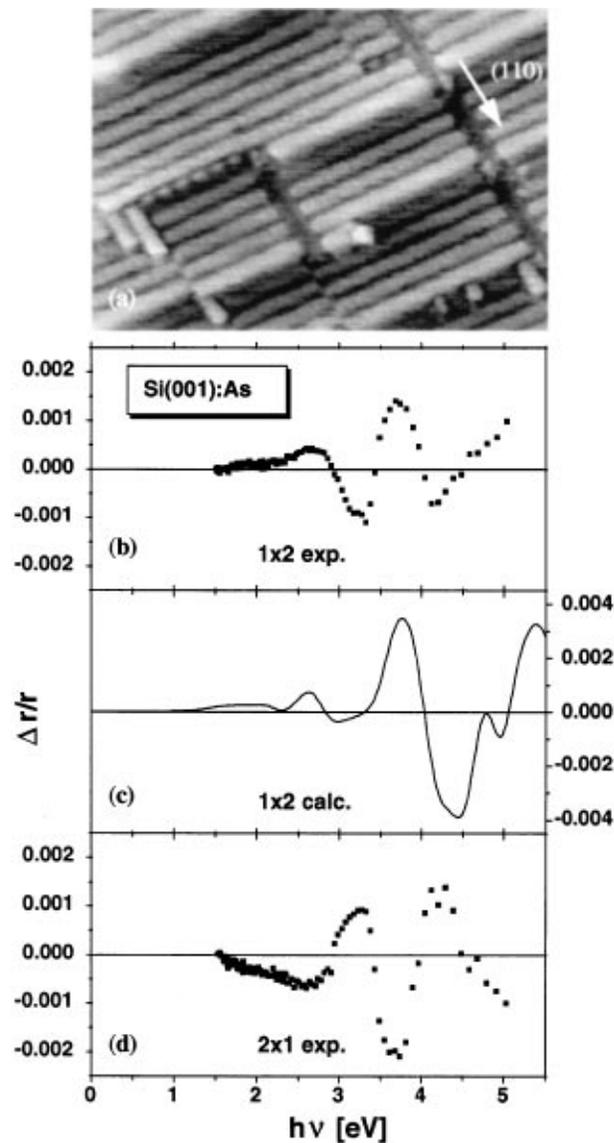
FIG. 1.   (a) Filled state STM image of As-terminated, vicinal Si(001):As-(1 × 2). Sample bias was –1.5 V and tunneling current was 100 pA. As_4 was used to dose the sample at room temperature through 600 °C. (b) RDS spectrum of the same surface. (c) Calculated $\Delta r/r$ for Si(001):As-(1 × 2). (d) RDS spectrum of similar sample dosed with As_4 at 500 °C to create the orthogonal Si(001):As-(2 × 1).

may be related to surface stress relief.)   Figure 1(b) is the corresponding RDS spectrum. Figure 1(d) shows the RDS spectrum for an As-terminated sample prepared using As$_4$, but with the bare Si surface first seeing arsenic when the surface is at 500 °C. We have shown [10] that this procedure produces a maximal coverage of (2×1) dimerization. Comparing Fig. 1(d) with Fig. 1(b) it is evident that the rotation of dimer orientation is observed in the RDS spectra, and that the dimers dominate the spectral features.

The spectrum calculated for the Si(001)-(1×2):As surface is shown in Fig. 1(c). Below 3 eV the RDS spectrum is very weak due to the absence of dangling bonds on the symmetric As-As dimers [11] of this passivated surface. The feature present at 2.7 eV arises from transitions between surface-perturbed bulk states and an antibonding σ^* state of the As-As dimer which is located about 2 eV above the valence band maximum. At higher energies (4.4 eV) there are strongly anisotropic transitions from the bonding to the antibonding σ states of the As-As dimer. However, these occur in the same energy region as transitions involving surface-perturbed bulk states and it is therefore difficult to assign the features above 3 eV to specific transitions between surface states. The agreement between the experimental and theoretical RDS obtained for this model system is clearly very good, thus demonstrating the accuracy of the calculations. However, as a cautionary note, the sensitivity of the RDS to details of the surface electronic structure, both surface states and surface-perturbed bulk states, implies that simple interpretation of RDS features, e.g., linking certain spectral features to As-As dimers whether on Si or GaAs, is not always possible.

Following these results for the As-terminated surface we now focus on the clean Si(001) surface. The atomic structure of this surface is more complicated and less ordered because of dimer buckling and dynamic flipping at RT. Figure 2(a) shows a filled state STM image of a bare, 4° vicinal Si(001) sample. The terraces and steps are evident as is the predominant orientation of dimer rows perpendicular to the terrace edges, the so-called (2×1) configuration. Occasional single height steps result in smaller terraces of (1×2) dimerization. The net area of (2×1) material is equal to the total area probed minus twice the area of rotated dimerization. Thus in Fig. 2(a) the net (2×1) coverage is 0.6. We find this coverage is typical of the bare, vicinal Si(001) prepared by annealing at 1030 °C. One should also note, in addition to the Si-Si dimers, the presence of missing dimer defects, pinned buckled dimer rows, and perhaps other inhomogeneities. Such inhomogeneities could conceivably play a complicating role in analyzing the origins of the RDS spectra.

The RDS spectrum for the same surface is shown in Fig. 2(b) (dots). It obviously manifests a significantly different signature from that of the As-passivated surface. At photon energies below 2 eV we observe a significant
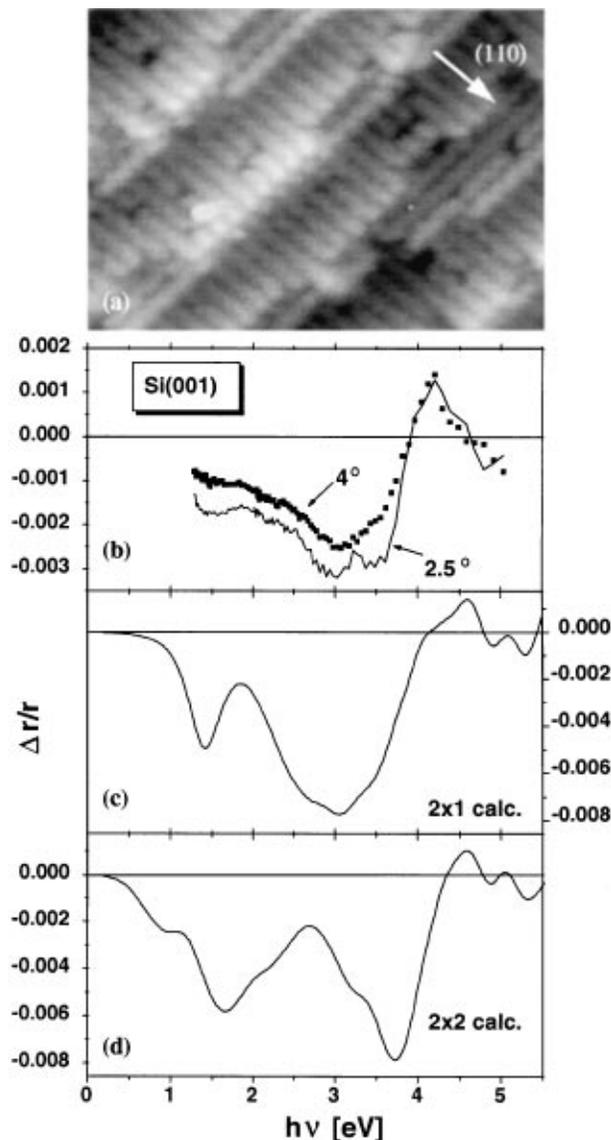
FIG. 2.   (a) Filled state STM image of bare, 4° vicinal Si(100). Sample bias was –1.5 V and tunneling current was 100 pA. The distance between dimer rows is 0.8 nm. (b) RDS spectrum of the same surface (dotted) and of a 2.5° vicinal surface (solid line). Calculated $\Delta r/r$ for the (c) 2×1 and (d) 2×2 geometries.

optical anisotropy due to the presence of dangling bonds on this surface. Also shown (solid line) is a spectrum for clean 2.5° vicinal Si(001). On this surface the terraces are wider than those on the 4° surface and we observe characteristic and reproducible enhancements of the RDS signal around 1.4 and 3.5 eV photon energy. At these energies the optical transitions involve unoccupied dangling bond states which is further corroborated by an extreme sensitivity to adsorbates.

The ground state of the Si(001) surface is the $c(4 \times 2)$ reconstruction, a structure in which the dimer buckling direction alternates along the row of dimers [12,13].

However at room temperature, where the RDS measurements are performed, the surface is not well ordered. Calculations have therefore been performed for two different structures: a 2×1 structure, which has all of the dimers buckled in the same direction, and a 2×2 buckled dimer structure, which has alternate dimer buckling along the dimer row, like the $c(4 \times 2)$ surface. The calculated equilibrium magnitude of buckling is 0.57 Å for the 2×1 and 0.68 Å for the 2×2. Comparison of the two spectra provides an indication of the sensitivity of the RDS spectra to dimer ordering.

The RDS spectrum calculated for the Si(001)-(2×1) surface, shown in Fig. 2(c), exhibits a peak at 1.4 eV which arises from transitions between the occupied and empty dangling-bond bands. The anisotropy appearing at higher energies originates from a number of sources, including transitions between occupied back-bond surface states and the empty dangling bond states. The result for the 2×2 surface is shown in Fig. 2(d). The differences between the spectra calculated for the 2×1 and 2×2 structures indicate that the RDS spectrum is sensitive to the dimer ordering. Below 2 eV the single peak in the 2×1 spectrum is replaced by a set of features which result from transitions between the zone-folded dangling-bond bands. Transitions between back-bond surface resonances and the empty dangling-bond states make strong contributions to the anisotropy occurring near 3.7 eV. Overall the comparison between theory and experiment is very good, especially when one considers that dimer ordering is certainly not complete at room temperature. An admixture of the 2×1 and 2×2 spectra could be employed to approximate the theoretical response for the actual sample configuration.

It is interesting to compare the present calculations of $\Delta r/r$ for Si(001)-(2×1) to the tight-binding calculations performed previously by Shkrebtii and Del Sole [14]. The most significant difference is that the peak originating from the transitions between the occupied and empty dangling-bond derived bands, which occurs near 1.4 eV, is opposite in sign to that obtained in the tight-binding calculations. Our results indicate that the reflectivity is largest for light polarized perpendicular to the dimer bond, in agreement with the experimental results shown in Fig. 2. Our results, both experimental and theoretical, are in contrast to simple arguments based on the symmetry that the initial and final states would have in a local molecular orbital picture [2,14]. This highlights the necessity of performing an accurate calculation of the electronic structure and integration over the Brillouin zone to properly interpret RDS. It is clear that RDS

spectra are sensitive to the ordering of the dimer buckling. Thus one may expect the measurements for the Si(001) surface to be sensitive to temperature. In particular, as the temperature is lowered to the point where the 2×2 or $c(4 \times 2)$ ordering is present over a substantial fraction of the surface, one expects to observe the anisotropy in the transitions between occupied and empty dangling bonds at energies as low as 1 eV.

In conclusion, we have measured RDS spectra under controlled experimental conditions for the bare and As-terminated Si(001) surfaces and have shown that the measured spectra can be understood in terms of calculated transitions involving the surface electronic structures. For Si(001):As, a model system with a well-defined atomic structure, we obtain excellent agreement between theory and experiment. We identify spectral features related to dimer surface states. For the bare Si(001) surface we have identified a peak in the RDS spectra near 1.4 eV with transitions between occupied and empty dangling bonds on the Si-Si dimers. The close correspondence between theory and experiment demonstrates that the local atomic structure imaged by STM can be linked to the measured RDS spectra by calculations of the surface electronic structure.

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