

Nanowire-induced optical anisotropy of the Si(111)-In surface

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Ab initio calculations of the reflectance anisotropy of Si(111)-In surfaces are presented. A very pronounced optical anisotropy around 2 eV is predicted for the structural model proposed by Bunk *et al.* [Phys. Rev. B **59**, 12 228 (1999)] for the (4×1) reconstructed surface. The $(4\times 2)/(8\times 2)$ reconstructed surface, induced by a slight distortion of the indium chains, is shown to result in a splitting of the 2 eV peak. The calculated results are in excellent agreement with recent polarized reflectance data acquired during the $(4\times 1)\rightarrow(4\times 2)/(8\times 2)$ phase transition.

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I. INTRODUCTION

Indium may self-assemble on Si(111) in a (4×1) pattern that is formed by long rows of In atoms. The study of this reconstruction goes back to the 1960's,¹ but has intensified recently. On one hand, the chains formed by the In atoms may be the smallest known atomic wires in existence,^{2,3} which makes them interesting in the technological context of downsizing the microelectronics into the nanoscale regime. On the other hand, one-dimensional electronic systems are expected to show interesting electronic features, such as spin-charge separation in a Luttinger liquid or Peierls instabilities (see, e.g., Ref. 4). Indeed, the metallic (4×1) phase of the In chains was found to undergo a reversible Peierls-like transition below room-temperature, where the period along the chain is doubled, forming (4×2) and finally (8×2) reconstructions.^{5,6}

On the basis of surface x-ray diffraction (SXRD) data⁷ a detailed structural model for the Si(111) (4×1) -In surface has been developed, which also accounts for previous experimental findings. Its main features are zigzag chains of Si atoms alternating with zigzag rows of In atoms on top of an essentially bulklike Si lattice [see Figs. 1(a) and 1(b)]. The Si chain is thus similar to the π -bonded chain of the Si(111) $\times(2\times 1)$ reconstruction. Strong support for this structural model comes from a series of *first-principles* calculations.⁸⁻¹⁰ The calculations not only confirmed the experimentally determined surface geometry, but also reproduced the dispersion of the measured surface electronic states² and the experimentally detected image state anisotropy.¹¹ SXRD has also been used to study the low-temperature (LT) Si(111)-In surface.¹² It was proposed that the periodicity along the In chains doubles, due to trimer formation of the outer indium atoms. In addition, a glide line occurs, causing a doubling of the unit cell in the direction perpendicular to the chains. The resulting (8×2) reconstructed surface structure is somewhat in contrast to the atomic configuration changes upon cooling inferred from LT photoemission data:¹³ Yeom and co-workers concluded that the inner In rows are mainly affected by the $(4\times 1)\rightarrow(4\times 2)/(8\times 2)$ phase transition. However, this is not in agreement with *ab initio* calculations. Cho *et al.*⁹ find that the outer indium chain atoms are displaced to form pairs, which are arranged in (4×2) or (8×2) symmetries as

shown in Figs. 1(c) and 1(d), respectively. The calculated structures for the $(4\times 2)/(8\times 2)$ reconstruction agree in many but not all respects with the interpretation of the SXRD data in Ref. 12. Discrepancies also exist regarding the electronic structure of the LT phase of the Si(111)-In surface. While some experimental studies find this phase to be

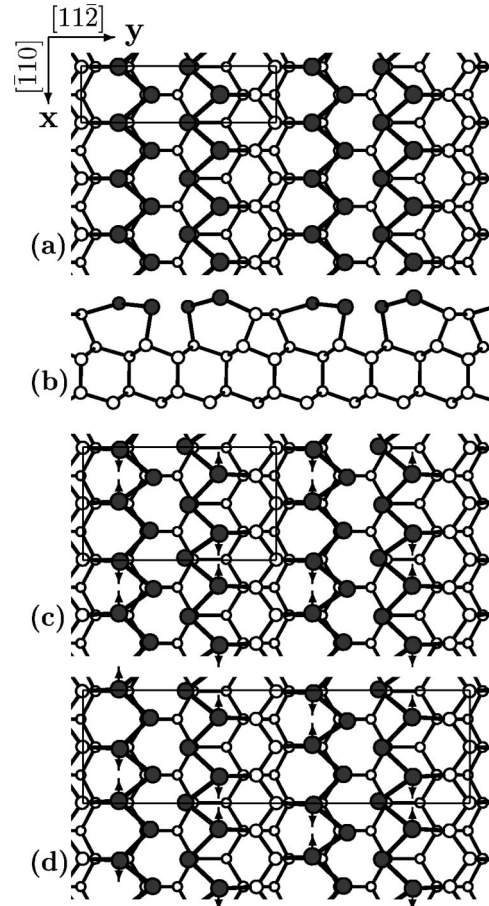


FIG. 1. Optimized atomic structures of the zigzag-chain model of the Si(111)-In surface: (a) top and (b) side view of the (4×1) reconstruction, (c) and (d) are the top views of (4×2) and (8×2) reconstructions, respectively. The solid/open circles are In/Si atoms. Surface unit cells are indicated. Arrows in (c) and (d) show the slight distortions of the outer indium atoms with respect to the (4×1) reconstruction.

insulating,^{3,5} others see only a reduced density of states at the Fermi level^{13,14} or remain inconclusive.¹⁵ *First-principles* calculations by the Kleinman group⁹ find no gap opening at the Fermi level as a result of the $(4 \times 1) \rightarrow (4 \times 2)$ phase transition. It is not clear, however, if this is indeed a correct finding or an artifact of the calculation, due to either the band gap underestimation in density-functional calculations,¹⁶ or an assumption of a wrong atomic structure for the LT phase of the Si(111)-In system.

Reflectance anisotropy spectroscopy (RAS) at the Si(111)(4×1)-In surface¹⁷⁻¹⁹ shows an optical anisotropy in the energy region of 2 eV, which is significantly larger than previously reported for any semiconductor system. Very recently, it has been found that this anisotropy splits into two peaks, at 1.9 and 2.2 eV, upon formation of the LT phase of the Si(111)-In surface.²⁰ In this paper we present *first-principles* calculations for the nanowire-induced optical anisotropy of the Si(111)-In surface. It will be shown that the atomic structure proposed from SXRD data in Ref. 7 for the In induced (4×1) symmetry explains very well the optical anisotropy measured for the room-temperature phase of the Si(111)-In surface. Our total-energy and RAS calculations strongly support Kleinman's model⁹ for the $(4 \times 2)/(8 \times 2)$ reconstructed Si(111)-In surface.

II. METHODOLOGY

The calculations employ a massively parallel real-space multigrid implementation²¹ of the density functional theory (DFT) within the local density approximation (LDA).²² The electron-ion interactions are described by nonlocal, norm-conserving pseudopotentials.²³⁻²⁵ A partial core correction to the In pseudopotential was added in order to take into account a nonlinear effect for the exchange-correlation term.²⁶ The spacing of the grid used to map the wave functions, the potentials and the charge density is 0.166 Å, corresponding to an energy cutoff of about 47 Ry in plane-wave calculations. The Si(111)-In surface is simulated by a periodic supercell that contains ten Si layers, one adsorbate layer, and a vacuum region corresponding in thickness to eight Si layers. Hydrogen atoms are employed to saturate the dangling bonds of the silicon atoms in the bottom layer. We use the calculated equilibrium lattice constant of 5.43 Å for silicon. Sets of special \mathbf{k} points corresponding to 32 points in the full (1×1) surface Brillouin zone were used for the self-consistent electronic structure calculations.

The atomic surface structure gives rise to corrections ΔR in the Fresnel reflectivity R_0 , which can be calculated from the diagonal slab polarizability components α_{ii} and the bulk dielectric function ϵ_b by

$$\frac{\Delta R(\omega)}{R_0(\omega)} = \frac{16\pi d \omega}{c} \text{Im} \left[\frac{\alpha_{xx}(\omega) - \alpha_{yy}(\omega)}{\epsilon_b(\omega) - 1} \right],$$

where d is the slab thickness, ω is the frequency, and c the speed of light.^{27,28} Here x and y are the directions parallel and perpendicular to the indium chain, respectively, i.e., the $[\bar{1}10]$ and $[11\bar{2}]$ directions. The surface dielectric function calculations were performed with uniformly distributed \mathbf{k}

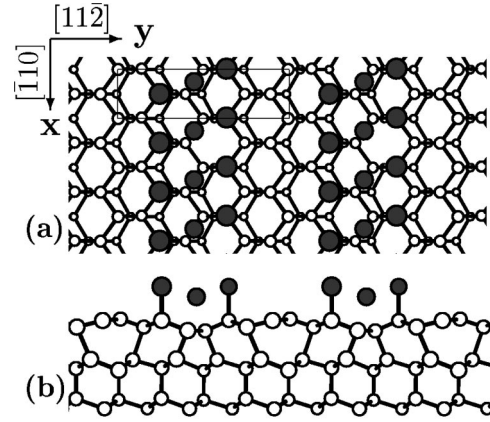


FIG. 2. The optimized atomic structure of the π -bonded chain stacking-fault model for Si(111) 4×1 -In reconstruction. Solid circles are In atoms and open circles are Si atoms. The (4×1) unit cell is indicated.

points corresponding to a density of 960 sampling points in the full (1×1) surface Brillouin zone. A linear cutoff function was used to eliminate spurious optical anisotropies from the bottom layer of the slab.²⁹ The dielectric function of metallic systems contains contributions from interband and intraband transitions.³⁰ The interband transitions dominate the spectra in the energy range usually investigated with RAS. Therefore, and because the intraband contributions are hardly accessible to *ab initio* calculations for systems of the size studied here, we consider only the interband part. It is calculated in the independent-particle approximation, i.e., neglecting excitonic and local-field effects. A scissors operator approach has been used to account for the band-gap underestimation of 0.5 eV for bulk Si due to the neglect of self-energy effects within DFT-LDA. Calculations for smaller systems^{31,32} have shown that many-body effects alter RAS spectra quantitatively rather than qualitatively, because RAS spectra are difference spectra, which are furthermore normalized to the bulk dielectric function. Therefore, calculations within the independent-particle approximation reliably reproduce experimental data for a wide range of semiconductors.^{33,34}

III. RESULTS AND DISCUSSION

The first reported RAS measurement of the Si(111)-In surface¹⁷ was interpreted in terms of a π -bonded chain stacking-fault (π -SF) model of the (4×1) reconstruction. This model, shown in Fig. 2, was proposed on the basis of Auger spectroscopy, low-energy electron diffraction, and scanning tunneling microscopy.³⁵ The substrate Si atoms form 7656 rings, i.e., two sixfold, one sevenfold, and one fivefold rings per unit cell. The In atoms on top form ridges containing three rows of In atoms. The edge In atoms saturate the dangling bonds of the underlying Si atoms and the central In row forms metallic bonds with the In atoms of the edge rows. We calculate an In-Si bond length of 2.66 Å. The minimum distance between In atoms amounts to 2.98 Å. The calculated optical anisotropy of the π -SF model is shown in Fig. 3. The RAS spectrum is negative for the complete en-

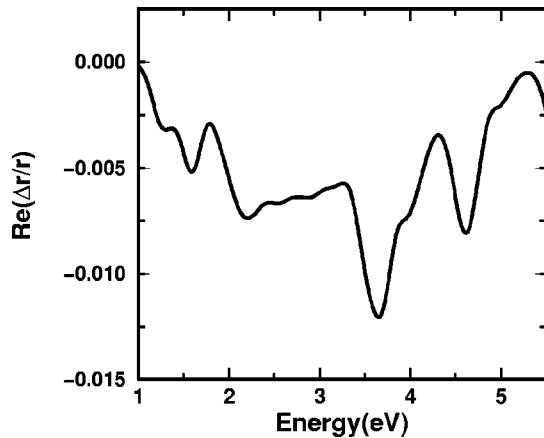


FIG. 3. RAS spectrum calculated for the π -SF model of the (4×1) -In reconstruction shown in Fig. 2.

ergy range considered, i.e., from 1.0 to 5.5 eV. While the sign and the magnitude of the calculated optical anisotropy agree with experiments,^{17–20} there is no agreement concerning the line shape and the energy positions of the RAS peaks. Experimentally, one very pronounced optical anisotropy dip at around 2 eV is observed. In contrast, the π -bonded chain stacking-fault model yields a series of features with the main peak at around 3.6 eV. From the calculated RAS spectrum we can thus exclude the π -SF model as the structure for In-induced (4×1) reconstructions of Si(111).

We therefore focus on the zigzag-chain model developed for interpretation of SXRD data of the Si(111) (4×1) -In surface.⁷ Here, four indium atoms and two Si atoms per (4×1) unit cell are adsorbed on an essentially bulklike (111) substrate surface, forming chains along the $[\bar{1}10]$ direction. Starting from the experimentally determined coordinates, total-energy minimization yields the structure shown in Figs. 1(a) and 1(b). The relaxed geometry is in good agreement with the experimental data⁷ and previous calculations.^{8–10} The In-In bond lengths within the chains amount to 2.98 and 3.00 Å. This is slightly larger than the sum of In covalent radii of 2.88 Å, but shorter than the 3.25 Å In-In distance in tetragonal bulk In, indicating the predominantly covalent character of bonding within the In chains. The distance between indium atoms in neighboring chains is 3.16 Å and the In-Si bond lengths are 2.68 Å. The calculated electronic structure of the Si(111) (4×1) -In surface confirms earlier experimental^{2,36} and theoretical results.^{8–10} There are three metallic bands crossing the Fermi level along the direction parallel to the atomic chains, which show only a weak dispersion perpendicular to the In chains.

The anisotropy of the surface electronic structure is reflected in the calculated optical anisotropy, shown in Fig. 4. Similarly to the results obtained for the π -SF structure, we find the RAS to be negative for nearly the complete energy range considered. In the case of the zigzag-chain model, however, a very strong anisotropy peak of 2.2% is calculated for a photon energy of 2 eV. This is in excellent agreement with the experimental findings^{17–20} of a very pronounced anisotropy of 1.2–2.0% at 2 eV. The fact that the calculated optical anisotropy is slightly larger than measured is ex-

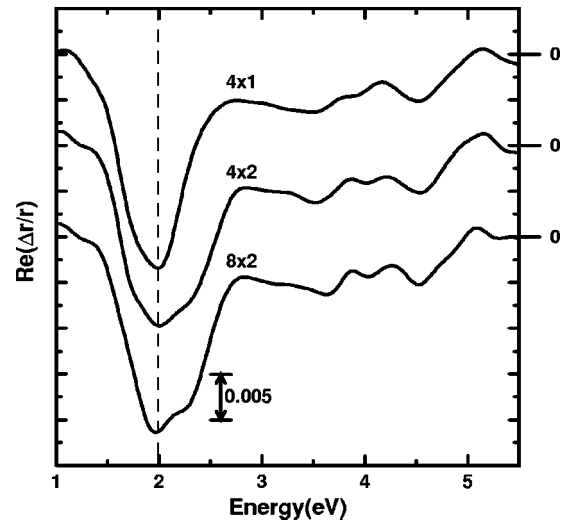


FIG. 4. RAS spectra calculated for the zigzag-chain models of the Si(111)-In surface reconstructions shown in Fig. 1. The curves are shifted vertically for clarity, with the zero position indicated on the right. The scale is shown in the inset.

pected. Our results refer to a single-domain Si(111)-In surface free of steps and other defects. Defects in the In chains and signals from minority domains reduce the peak at 2 eV, whereas surface steps give rise to additional features at the bulk critical points of Si, i.e., at 3.5 and 4.3 eV.³⁷ The optical anisotropy at 2 eV is unambiguously attributed to surface states, because this energy region is far below the direct optical gap of Si. However, it is not directly related to the metallicity of the nanowires, which at low frequencies is expected to result in a stronger optical coupling for light polarized in the chain direction rather than perpendicularly to the chains. Therefore, the quasi-one-dimensional metallicity of the In chains should lead to positive optical anisotropies, which are indeed observed for photon energies below 1 eV.¹⁹ Our calculations cannot safely be extended to that energy region, because of the neglect of intraband transitions.

In order to calculate the structure of the LT phase of the Si(111)-In surface, we start from symmetry-distorted geometries with (4×2) and (8×2) translational periodicities. The resulting (4×2) and (8×2) structures, shown in Figs. 1(c) and 1(d), are mainly characterized by a pairing of the outer In chain atoms. Their distance is reduced from 3.84 Å in the (4×1) structure to 3.55 Å. This reconstruction mechanism agrees with the findings of the Kleinman group,⁹ who predict a corresponding reduction from 3.87 to 3.59 Å. The pairing leads to an alternating relaxation of the inner chain atoms towards or away from the center of the neighboring indium chain. However, the pairing-induced In-In and In-Si bond length changes are hardly discernible, i.e., below 0.02 Å. The calculated band structures for the (4×2) and (8×2) have no gap at the Fermi level. This may partially be related to the band gap underestimation typical of DFT-LDA calculations.¹⁶ It appears likely that self-energy effects open a small gap for the lowest lying metallic band (see S_3 in Fig. 2 in Ref. 9), because this band nearly bisects the (4×1) surface Brillouin zone. Therefore, the corresponding Fermi surface has the possibility of nesting, potentially driving the

opening of a Peierls gap. This mechanism is hardly plausible, however, because of the remaining metallic surface states. Our calculations, which are in agreement with the *first-principles* results of Cho *et al.*,⁹ thus support the view that the doubling of the surface unit cell results in a reduction of the density of states at the Fermi level, but not in the opening of a fundamental gap. This is in agreement with some but not all of the recent experimental studies.^{13,14}

In order to verify the calculated structural models for the $(4 \times 2)/(8 \times 2)$ phase, we calculated their reflectance anisotropy, see Fig. 4. The spectra are similar to the one calculated for the (4×1) phase. However, for the (4×2) reconstruction a shoulder at 2.2 eV emerges, which is even more pronounced for the (8×2) surface. It corresponds exactly to the optical signature of the $(4 \times 1) \rightarrow (4 \times 2)/(8 \times 2)$ phase transition found in a recent experimental study.²⁰ In addition to the appearance of the 2.2 eV shoulder, the calculated minimum of the RAS shows a slight redshift by about 0.1 eV. Again, nearly quantitative agreement with the experimentally observed shift from 1.96 to 1.90 eV is obtained. Fleischer *et al.*²⁰ argue that the measured changes in the optical anisotropy cannot be explained as a temperature-induced sharpening of the original 2 eV peak, since the overall width of the structure is much larger for the LT phase. The changes of the RAS spectra can thus only be explained by electronic and structural modifications of the Si(111)-In surface accompanying the $(4 \times 1) \rightarrow (4 \times 2)/(8 \times 2)$ phase transition. The excellent reproduction of these changes in the calculated surface optical properties is a very strong indication for the

correctness of the underlying surface structural model, i.e., the geometry originally proposed by Kumpf and co-workers¹² and modified by Cho *et al.*⁹

IV. SUMMARY AND CONCLUSIONS

The optical anisotropies for different models used to explain the formation of In nanowires at the Si(111) surface have been calculated from *first principles*. A comparison with measured data strongly supports the zigzag-chain model for the room-temperature (4×1) reconstructed phase of the Si(111)-In surface. An energetically favored pairing of In atoms gives rise to a doubling of the periodicity along the chain direction. The energy can be further lowered by arranging neighboring chains in a (8×2) superstructure. These structural changes are accompanied by changes in the calculated optical anisotropy which are in excellent agreement with data acquired during the formation of the low-temperature phase of the Si(111)-In surface. Our results for the surface electronic structure are compatible with the view that a reduction of the density of states at the Fermi level occurs upon the $(4 \times 1) \rightarrow (4 \times 2)/(8 \times 2)$ phase transition. However, there is no indication of gap opening.

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