

Optical anisotropy of Si(111)- (4×1)/(8×2)-In nanowires calculated from *first-principles*

S. Wippermann^{*1}, W. G. Schmidt¹, F. Bechstedt², S. Chandola^{3,4}, K. Hinrichs³, M. Gensch³, N. Esser³, K. Fleischer⁴, and J. F. McGilp⁴

¹ Lehrstuhl für Theoretische Physik, Universität Paderborn, 33095 Paderborn, Germany

² Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität, Max-Wien-Platz 1, 07743 Jena, Germany

³ ISAS-Institute for Analytical Sciences, Department Berlin, Albert-Einstein Str. 9, 12489 Berlin, Germany

⁴ School of Physics, Trinity College Dublin, Dublin 2, Ireland

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* Corresponding author: e-mail Wippermann@phys.uni-paderborn.de, Phone: +49-5251-60-2332, Fax: +49-5251-60-3435

First-principles calculations of the anisotropic optical response of Si(111)-(4×1)(8×2)-In from the mid-infrared to the visible region are compared with recent experimental data. The experimental data show that the anisotropic Drude tail of the (4×1) room-temperature phase is replaced by two peaks at 0.50 eV and 0.72 eV after the phase transition to the low-temperature (8×2) structure took place.

The spectrum calculated from both intraband and interband transitions for the metallic zig-zag chain model of the (4×1) phase accounts well for the room-temperature data. The low-temperature data are well explained on the basis of the semiconducting hexagon (8×2) model by interband transitions mainly from a region close the $\bar{X}\bar{M}$ high-symmetry line of the Brillouin zone.

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One-dimensional (1D) electronic systems are attracting considerable interest for both fundamental and technological reasons. The ordered array of In nanowires that self-assembles at the Si(111) surface to form the Si(111)-(4×1)-In phase, which has quasi-1D metallic properties at room temperature (RT), is an intensively investigated model system for one-dimensional (1D) electronic systems. Results from many different experiments, as well as *ab-initio* calculations, agree that the In atoms form two parallel metallic zig-zag chains, which are separated by zig-zag Si chains that resemble the π -bonded chains of Si(111)-(2×1) (cf. Fig. 1c) [1–10]. The structure exhibits three quasi-1D surface state bands, which cross the Fermi level and disperse strongly along the chain direction, and show only a weak dispersion perpendicular to the chain.

Yeom *et al.* [12] reported that Si(111)-(4×1)-In undergoes a reversible phase transition below 120 K to an (8×2) structure, with a strong reduction of the density of states at the Fermi level. However, the low temperature

(LT) ground-state with its associated properties remains controversial [9]. While the RT (4×1) phase is a quasi-1D metal [8, 13, 19], it has been variously suggested that the LT (8×2) phase is metallic, but with a lower density of states at the Fermi level [16, 17, 20], semimetallic [16], and semiconducting with a fundamental energy gap of 0.1–0.3 eV [12–15, 18]. Most *ab-initio* studies predict the nanowire ground state to be characterized by the formation of In trimers (cf. Fig. 1b) and find no gap opening [3, 4, 6]. Recently, however, a structure with In hexagons, arising from both trimerisation and shear distortions in neighbouring chains (Fig. 1a), has been predicted, which is semiconducting [21]. Total-energy calculations [9] of the hexagon and the trimer model for the LT phase found the energy differences between the competing structures to be very small and to depend on the approximations made in the calculations, e. g., the treatment of the In 4d states, and exchange and correlation effects. Cho and Lee [22] state that

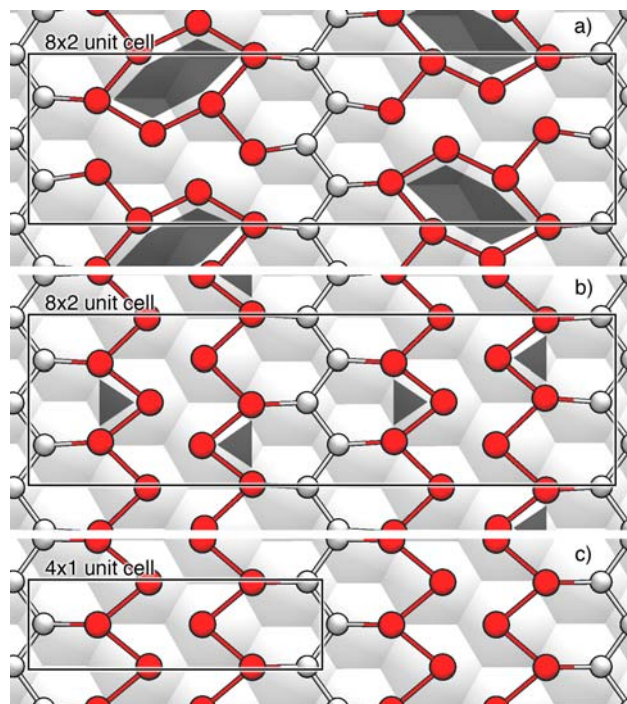


Figure 1 Schematic top views of the a) hexagon and b) trimer model of the LT Si(111)-In nanowire array and the c) ideal Si(111)-(4×1)-In reconstruction, respectively.

the hexagon model is not stable, but the model has been supported recently by positron diffraction studies [23].

Given these ambiguities, optical spectroscopy may be helpful. The small differences in geometry of the trimer and hexagon model lead to significant changes in the band structure near the Fermi level [9,21]. Direct optical transitions in this energy region, as probed by infrared (IR) reflection anisotropy spectroscopy (RAS), are very sensitive to such changes. In fact, the present authors have previously shown that RAS spectra simulated on the basis of the trimer and the hexagon model for the LT (8×2) phase differ strongly, in particular in the mid-IR region, with the latter being in excellent agreement with the measured data [11]. Due to the limited computer resources, however, the calculations in Ref. [11] had to be restricted to interband optical transitions. Here we demonstrate that *ab-initio* optical response calculations including both intraband and interband transitions for the metallic zig-zag chain model of the (4×1) phase account well for the measured room-temperature data [11].

The calculations are performed using density functional theory (DFT) within the local density approximation (LDA) as implemented in VASP [29]. The In 4*d* states are treated as core electrons. The Si(111)-(4×1)/(8×2)-In surfaces are modeled by repeated symmetric slabs with 6 Si bilayers and a vacuum region equivalent in length. The **k**-space integrations are performed using uniform meshes equivalent to 64 and 960 points in the (1×1) surface Brillouin zone for electronic structure and optical response calculations, respectively.

The reflection anisotropy $\Delta R/R$ for light polarized along α and β can be derived from a slab calculation and is given by

$$\frac{\Delta R}{R} = \frac{4\omega d}{c} \text{Im} \left\{ \frac{4\pi[\alpha_{\alpha\alpha}(\omega) - \alpha_{\beta\beta}(\omega)]}{\epsilon_b(\omega) - 1} \right\} \quad (1)$$

where $\epsilon_b(\omega)$ is the bulk dielectric function, and $\alpha_{\alpha\alpha}$ and $\alpha_{\beta\beta}$ are components of the optical polarizability tensor of the slab with thickness d [24]. We calculate the slab polarizability in the independent-particle approximation based on the electronic structure obtained within DFT-LDA.

The calculation of intraband contributions to the slab polarizability requires the introduction of a small **q** vector, with the optical transitions proceeding along $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{q}$. The Drude contribution from the intraband transitions is then obtained in the limit $\mathbf{q} \rightarrow 0$. In the numerical evaluation of the *intraband* contributions the **k**-point sampling and the chosen **q** vector become two extremely critical convergence parameters. A sufficiently small **q** vector must be ensured to reproduce the $\mathbf{q} \rightarrow 0$ limit. However, this simultaneously enforces a correspondingly dense **k**-point mesh. In the present study the **k**-space integrations to calculate the intraband contributions is performed using a uniform mesh equivalent to 30 720 points in the (1×1) surface Brillouin zone. The chosen **q** vectors are $\mathbf{q} = |0.0125|$ and $\mathbf{q} = |0.0417|$ along and perpendicular to the nanowire direction, respectively. For the numerical calculation we use the DP code by V. Olevano, L. Reining and F. Sottile [30]. Due to the enormous computational requirements, these calculations could only be performed for the ideal Si(111)-(4×1) reconstruction and not for any larger reconstruction.

Fig. 2 shows measured and calculated RAS spectra. The experimental data reveal a dramatic difference between the RT (4×1) and LT (8×2) phases. There is a smooth Drude-like increase to lower energies and no interband transitions below 1 eV for the RT (4×1) phase. This is in contrast to the behaviour above 1 eV, where the optical response is dominated by interband transitions [26,27]. The larger Drude-like response parallel to the chains arises from the highly anisotropic conductivity of this surface, as measured by four-point probe STM [8,13].

The LT (8×2) phase shows two sharp positive peaks at 0.50 and 0.72 eV, while the low energy Drude tail is removed. Its replacement by these peaks indicates a metal-insulator transition. There is no evidence of residual metallic behaviour in the (8×2) phase in the mid-IR regime. Positive anisotropy indicates that optical transitions parallel to the chains are dominant in this spectral region. Both phases show the broader negative 1.9 eV feature, which splits below the MI transition [4,26,27]. The calculated anisotropy of the ideal (4×1) reconstruction agrees well with experiment, provided intraband contributions are taken into account.

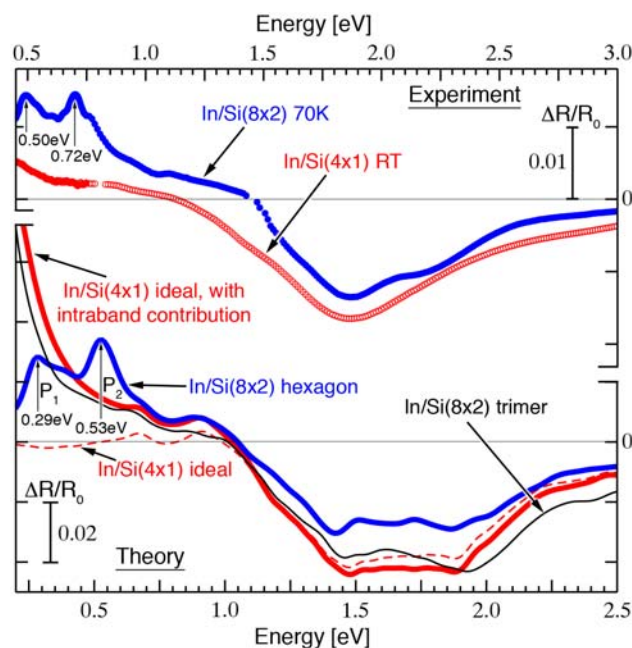


Figure 2 RAS spectra of Si(111)-(4×1) at RT (300 K) and Si(111)-(8×2) at LT (70K): upper, experiment; lower, theory. Note the different scales.

While no intraband transitions were calculated for the trimer model of the (8×2) LT phase, the RAS still shows a steep rise in analogy to the Drude-like behaviour of the (4×1) RT phase. This results from the increased density of states near the Fermi level due to band folding effects. However, since this model exhibits only one band crossing the Fermi level – with low dispersion – we expect the contribution of the intraband transitions to be almost negligible for the trimer model.

The calculated anisotropy of the semiconducting hexagon model of the (8×2) structure, on the other hand, agrees well with the low-temperature experiment, as has

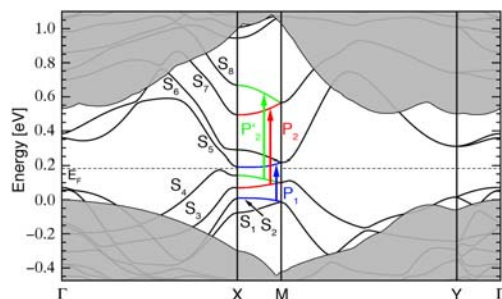


Figure 3 Band structure of the hexagon model for Si(111)-(8×2)In calculated within DFT-LDA. Pronounced optical transitions showing up in the RAS spectra as the peaks P_1 and P_2 in Fig. 2 are marked. Gray regions correspond to the projected Si bulk bands. The bulk valence band maximum is chosen as energy zero. The Fermi level is indicated.

been reported previously [11]. Below 0.7 eV two positive peaks are calculated, separated by 0.24 eV. This splitting agrees very well with the experimental splitting of 0.22 eV. Detailed comparison reveals that the calculated mid-IR peaks are redshifted by about 0.25 eV (note the different scales in Fig. 2). The underestimation of excitation energies is typical for DFT calculations where self-energy effects are neglected. However, the complexity and size of the In nanowire structure prevents the calculation of optical spectra using many-body perturbation theory that includes self-energy and excitonic effects [28]. Quasiparticle calculations for the high-symmetry points of the hexagon model surface band structure found self-energy effects to increase the lowest transition energies by 0.26 eV on average [9]. A larger shift of 0.5 eV, typical for Si excitation energies [28], applies to the higher energy negative optical anisotropies, because the optical transitions involve Si states [27]. Allowing for these energy shifts, the agreement between the calculated and measured RAS spectra is convincing.

The origin of the two peaks in the mid-IR regime can be traced to optical transitions close to the X and M points of the surface Brillouin zone, indicated by P_1 and P_2/P'_2 in Fig. 3, corresponding to the labels in Fig. 2. Around $\overline{XM}$, nearly parallel valence and conduction bands close to the Fermi level give rise to a high joint density of states.

However, not all of the relevant transitions arise from the region of the $\overline{XM}$ high-symmetry line, but from inside the Brillouin zone as well. To visualize these transitions a 3-dimensional representation of the surface Brillouin zone is shown in Fig. 4. The notation of the surface bands $S_1 - S_8$ and the peaks $P_1, P_2/P'_2$ refers to Fig. 3 and 2, respectively. The transitions indicated in Fig. 4 b/c) take place over the whole width of the Brillouin zone, while the transitions in d/e) occur either near the $\overline{TX}$ or $\overline{MY}$ high-symmetry lines only. It can also be seen that in some cases transitions from and to the same bands contribute to different peaks, as shown in Fig. 4 e). Transitions from $S_2 \rightarrow S_5$ contribute to either P_1 or P_2 , depending on the exact location of the transition inside the surface Brillouin zone.

In conclusion, *ab-initio* optical response calculations have been reported for the In-Si nanowire system. The calculated spectra support the picture of a metal-insulator phase transition between a metallic Si(111)-(4×1)-In phase formed by zig-zag chains of In atoms at room temperature and a semiconducting (8×2) phase characterized by In atoms forming hexagons.

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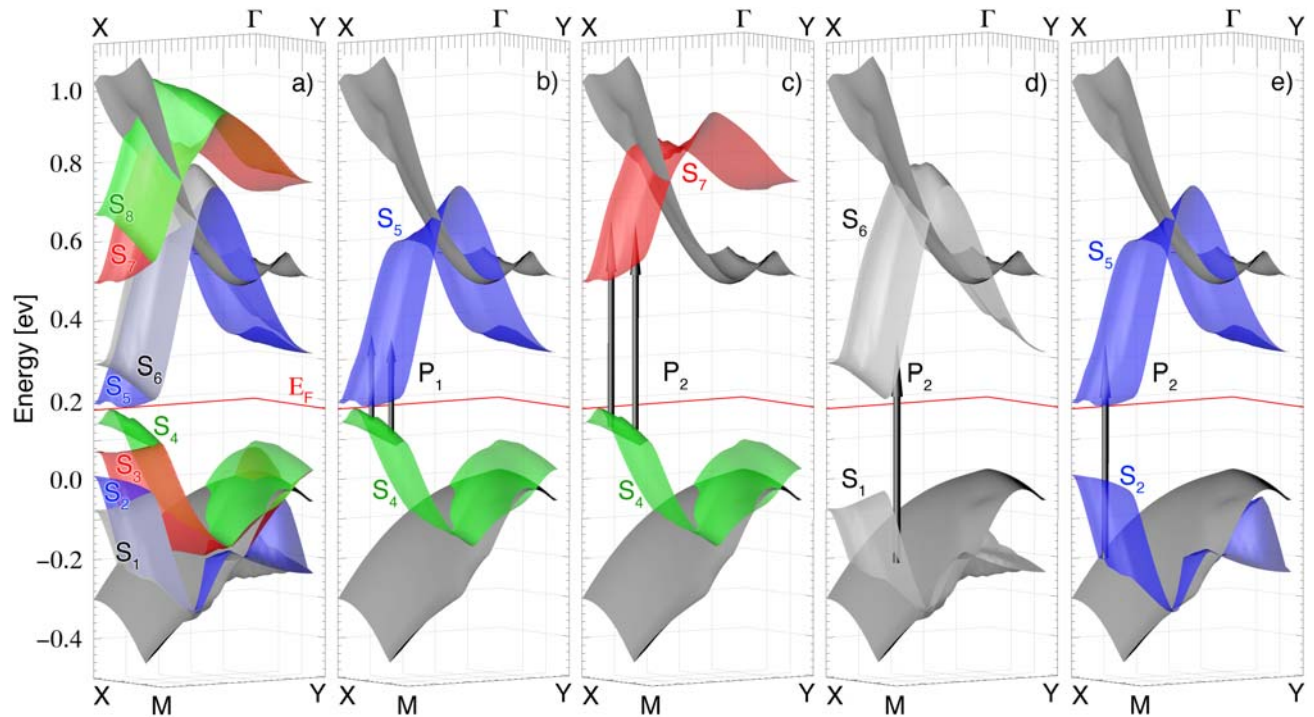


Figure 4 a) 3-D band structure of the hexagon model for Si(111)-(8×2)In calculated within DFT-LDA. The notation of bands is consistent with Fig. 3. Pronounced optical transitions from *within* the Brillouin zone causing the peaks P_1 and P_2 in the RAS spectra are shown in b) and c)-e), respectively. The Fermi level is indicated by E_F .

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