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Optical anisotropy of the In/Si(1 1 1)(4 × 1)/(8 × 2) nanowire array

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ABSTRACT

Ab initio calculations of the reflectance anisotropy of Si(1 1 1)-In surfaces are presented. A very pronounced optical anisotropy around 2 eV is found that is related to In-chain states. The distortion of the indium chains characteristic for the (4 × 1) → (8 × 2) phase transition results in a splitting of the 2 eV peak, as observed experimentally. The splitting occurs irrespective wether the phase transition occurs according to the trimer or hexamer model.

Quasi one-dimensional (1D) structures show interesting physical properties and have a large technological potential, e.g., for atomic-scale interconnects. Therefore there is an increasing interest in understanding and predicting the electronic properties of quasi-1D systems [1–4]. Highly anisotropic surface superstructures have found considerable interest in this context. The ordered array of In "nanowires" formed upon room temperature (RT) In monolayer deposition and subsequent annealing is probably the most intensively investigated system of this kind. By now, experiment and theory have established a structural model (see uppermost panel in Fig. 1) that is well accepted for the RT phase of the nanowire array [5–13]: each nanowire consists of two zigzag chains of In atoms within a (4 × 1) surface periodicity. The nanowires are separated by Si chains resembling the π-bonded chains of the clean Si(1 1 1)(2 × 1) surface.

The low-temperature (LT) structure of this system, however, and its properties are controversial: below about 125 K a reversible temperature-induced phase transition leads to a (8 × 2) surface periodicity clearly seen in STM [14–19]. It has been suggested that the transition is charge density wave driven by a single-band [14] or triple-band [16] Peierls instability or by a simple energy lowering due to a periodic lattice distortion [20,6,21,12,11]. While the RT (4 × 1) phase is a quasi-1D metal [22] that gives rise to electron transport attributed to In related surface states [23,15,22], many experimental studies conclude that the phase transition leads to a fundamental energy gap of 0.1–0.3 eV [14–17,24]. Others only state a reduced density of states at the Fermi energy (E_F) [20,25,18] or remain inconclusive [26].

Most *ab initio* calculations [6,9,11,12,21,13], predict the pairing of the outermost atoms in the zigzag subchains and the formation of trimers (cf. middle panel in Fig. 1). These structural changes open pseudogaps in the triple-band structure, but one surface band still crosses the Fermi level. Calculations by the Flores group [27,28] obtained a different surface ground state: shear distortions in neighboring In chains – indicated in Fig. 1 – allow for the formation of In hexagons in a (4 × 2) surface periodicity. This structure was found to be insulating. The hexamer model is supported by recent reflection high-energy positron diffraction studies [29,30].

A computational study [31] of the hexamer and the trimer model for the low-temperature phase concluded that an unambiguous identification of the internal structure of the LT phase on the basis of the total energy is problematic. The energy differences between the competing structures are very small and depend on numerical details as well as the approximations made in the calculations concerning, e.g., the treatment of the exchange and correlation effects and the In 4*d* states. Cho and Lee [32] explicitly state that the hexagon model is not stable.

Given the ambiguities of the total-energy calculations in determining the ground-state structure of the (8 × 2) phase, the comparison of fingerprints calculated for structural candidates with measured data may be helpful. Earlier we considered the electron transport properties [31,4] and found that the calculated conductance gives strong evidence for hexagon formation. On the other hand, the calculated optical anisotropies [9] for the (4 × 1) and the trimer-reconstructed (8 × 2) nanowire arrays are compatible with the measured evolution of the surface optical response during the (4 × 1) → (8 × 2) phase transition [10]: reflectance anisotropy spectroscopy (RAS) at the Si(1 1 1)(4 × 1)-In surface [33–35] shows an optical anisotropy in the energy region of 2 eV, which splits into two peaks, at 1.9 and 2.2 eV, upon formation of the LT phase of the

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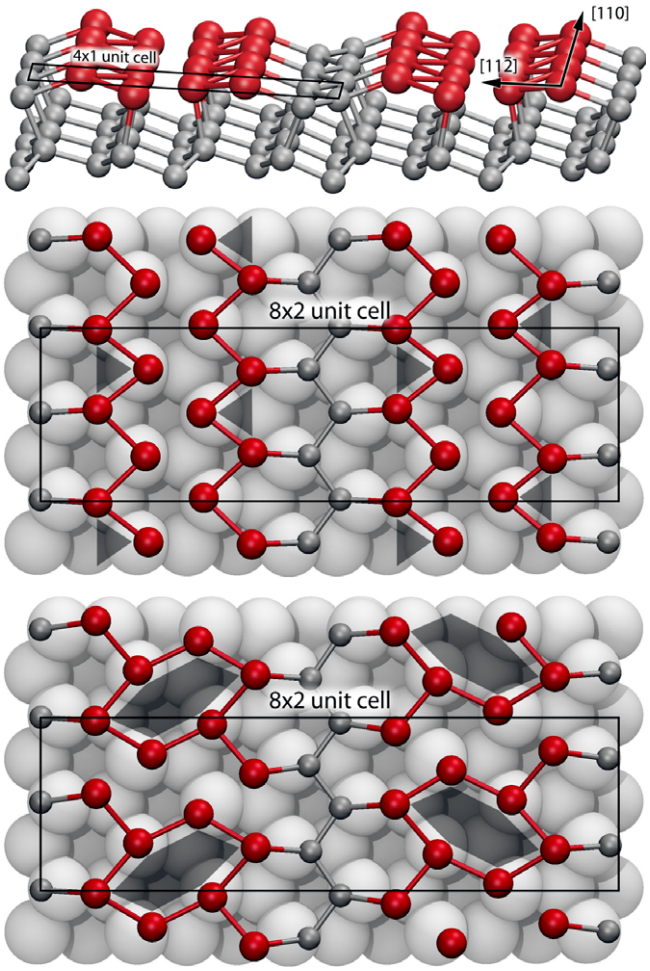

Fig. 1. Top views of the ideal, unreconstructed In/Si(1 1 1)(4 × 1) surface (upper panel) and the trimer and hexagon formation within 8 × 2 translational symmetry (middle and lower panel, indicated by shaded polygons).

Si(1 1 1)-In surface [10,36]. In order to help clarifying the structure of the In nanowire array, we present in the following calculations of the optical anisotropy of the Si(1 1 1)(4 × 1)-In surface and of the two structural models suggested for its LT (8 × 2) phase, i.e, the trimer and the hexagon model [28,31].

Our results are obtained using density functional theory (DFT) within the local density approximation (LDA) [37,38] for exchange and correlation as implemented in VASP [39]. The electron–ion interaction is described by the projector-augmented wave (PAW) potentials. The In 4*d* states are treated as core electrons. The In/Si(1 1 1)(4 × 1) and (8 × 2) surfaces are simulated by repeated symmetric slabs with 12 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.

As shown by Del Sole et al. [40,41], the reflection anisotropy $\Delta R/R$ for light polarized along α and β can be derived from a slab calculation and is given by

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

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. In the following we identify α and β with the [11$\bar{2}$] and [1 1 0] directions, respectively.

We calculate the slab polarizability in the independent-particle approximation based on the electronic structure obtained within DFT-LDA. A scissors operator is used to correct the band-gap underestimation. Thereby a constant shift of 0.5 eV is applied to all unoccupied DFT eigenvalues that lie more than 0.5 eV above the highest occupied electronic state. This ensures an approximate reproduction of the measured Si bulk band structure. For the energetically lower lying unoccupied states a linear interpolation up to a zero shift for states directly at the Fermi energy is used in order to model the energy dependence of the electronic self-energy. Beyond this crude approximation of the self-energy, many-body effects such as excitonic and local-field effects [42,43] are completely neglected. While this certainly results in a loss of quantitative accuracy and may strongly affect the calculated line shape, the past experience of the authors indicates that the calculated spectra can still be expected to be qualitatively reliable (see, e.g., Ref. [44]). This holds in particular if differences and trends for very similar systems are considered, as in the present case.

The calculated optical anisotropy is shown in Fig. 2. For all structural models we find the RAS to be negative for nearly the complete energy range considered. The spectra are dominated by a very strong anisotropy around 2 eV photon energies of about 3.6% and 4.8% for the (8 × 2) and (4 × 1) surface reconstructions, respectively. This is in excellent agreement with the experimental findings [33–35] of a very pronounced anisotropy of 2.4–4.0% (if the intensities are considered) at 2 eV. The fact that the calculated optical anisotropy is somewhat larger than measured is expected. Our results refer to a single-domain Si(1 1 1) surface free of steps and other defects that is covered with a perfect In nanowire array. Defects in the In chains and signals from minority domains present at the real surface may reduce the peak at 2 eV.

The optical anisotropy at 2 eV is necessarily related to surface states, because this energy is far below the direct optical gap of bulk 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 [10]. Our calculations cannot access that energy region, because of the neglect of intraband transitions that are unfortunately still too expensive for our computer resources. The negative anisotropy around 2 eV is related to a multitude of optical transitions perpendicular to the In chain direction that are either related to pure In chain states or involve the In–Si bonds. The for-

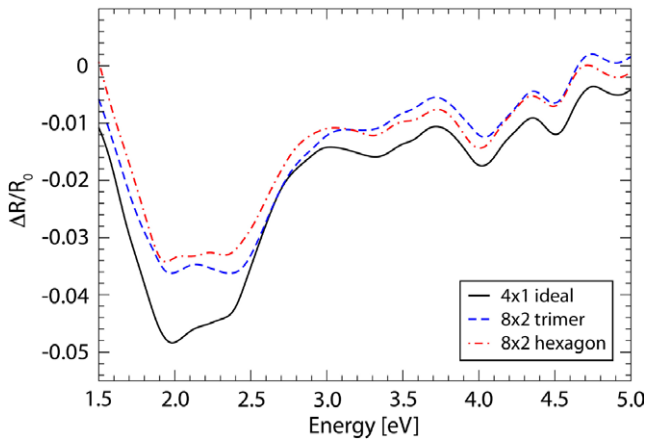

Fig. 2. RAS spectra calculated for the models of the In/Si(1 1 1) nanowire array shown in Fig. 1.

mer occur around 1.9 eV whereas the latter are observed at energies slightly above 2 eV. In Fig. 3 we show two representative transitions for the case of the (4×1) reconstructed nanowire array.

In order to assist in the identification of structural models for the (8×2) phase, we calculated the reflectance anisotropy for the hexamer and the trimer model, see Fig. 1. The spectra are similar to the one calculated for the (4×1) phase. However, the shoul-

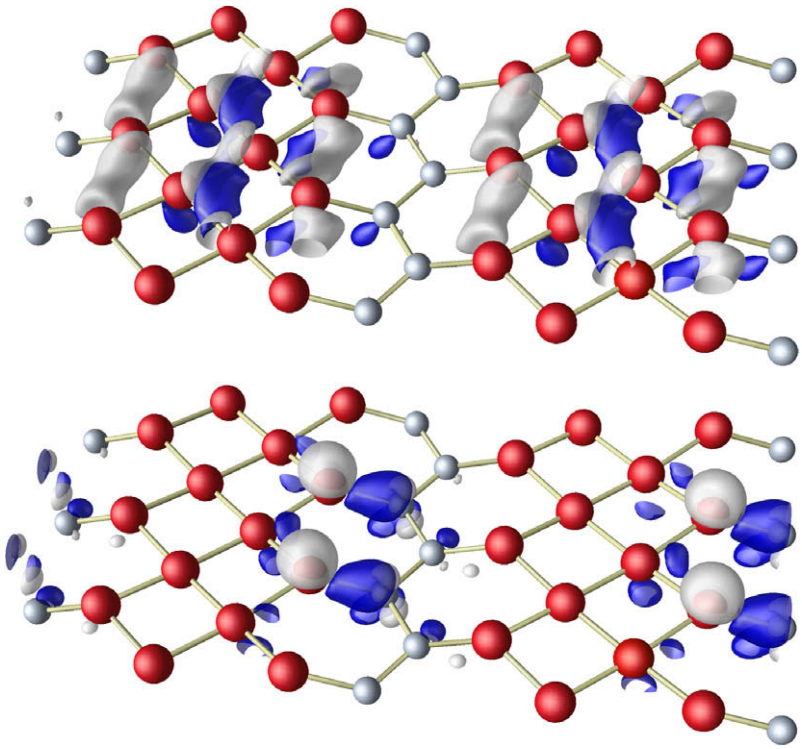

Fig. 3. Squared wave functions of surface electronic states that contribute strongly to the optical anisotropy of the In/Si(1 1 1)(4×1) nanowire array. The upper/lower panel shows the valence (dark) and conduction (light) states that cause an anisotropy at 1.9/2.2 eV. The isosurfaces are drawn for a density of 0.003 $Å^{-3}$.

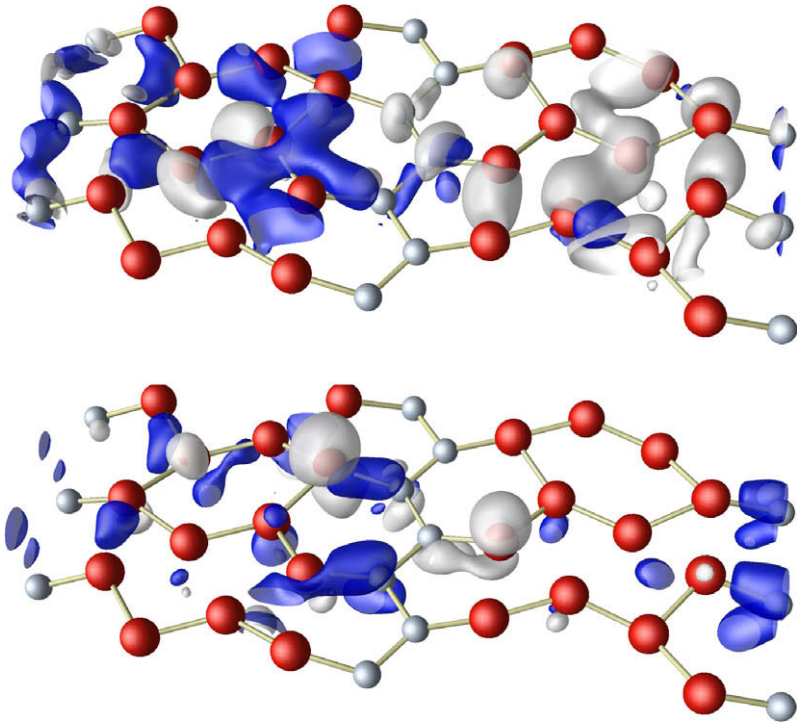

Fig. 4. Squared wave functions of surface electronic states that contribute strongly to the optical anisotropy of the In/Si(1 1 1)(8×8) nanowire array (hexamer model). The upper/lower panel shows the valence (dark) and conduction (light) states that cause an anisotropy at 1.9/2.2 eV. The isosurfaces are drawn for a density of 0.002 $Å^{-3}$.

der obtained for the (4×1) phase at around 2.4 eV develops into a separate peak for both models. Also, the optical anisotropy is reduced from about 4.8–3.6%. The splitting of the 2 eV anisotropy into two separate peaks corresponds exactly to the optical signature of the $(4 \times 1) \rightarrow (8 \times 2)$ phase transition found experimentally [10,36]. In addition to the peak splitting, the calculated minimum of the RAS shows a slight redshift by about 0.1 eV, which again is in very good agreement the experimental findings that state a shift from 1.96 to 1.90 eV during the phase transition. Fleischer et al. [10] 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 measured 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 In nanowire array accompanying the phase transition. Unfortunately, both the hexamer and the trimer model for the (8×2) phase give rise to a very similar optical anisotropy and – within the numerical accuracy of the present calculation – a discrimination of the models with respect to the degree of agreement with experiment is not possible.

Due to the fact that a multitude of electronic surface states is relevant for the occurrence of the optical anisotropy characteristic for the nanowire array – in fact, we find around 20 transitions to be relevant – it is impossible to provide a simple argument for the spectral changes accompanying the phase transition. We find that the symmetry reduction upon hexamer or trimer formation changes the orbital character of nearly all In chain related states and leads to a reduction of the oscillator strength of many transitions responsible for the overall larger optical polarizability perpendicular to the In chain direction. As an example, Fig. 4 shows the electronic states responsible for two optical transitions that lead to strong anisotropies for the case of the (8×2) hexamer-reconstructed nanowire array. The orbital character of these states is somewhat similar to the case of the ideal (4×1) nanowire array (cf. Fig. 3) and the respective optical transitions occur at similar energies. The transition matrix elements, however, are smaller by about one third.

To summarize, the optical anisotropies for ideal and hexamer as well as trimer reconstructed models for the In nanowire array at the Si(1 1 1) surface have been calculated from *first principles*. The comparison with measured data shows that the optical signatures of both the hexamer as well as the trimer model are very well suitable to explain the spectral changes acquired during the formation of the low-temperature phase of the In/Si(1 1 1) surface. Our calculations thus support the symmetry reduction of the In chains upon cooling, but do not allow predictions of the reconstruction model. In this respect, the extension of the optical measurements and calculations into the far infrared regime can be expected to be more conclusive.

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