

Atomic indium nanowires on Si(1 1 1): the (4×1) – (8×2) phase transition studied with reflectance anisotropy spectroscopy

K. Fleischer^{a,*}, S. Chandola^{a,c}, N. Esser^b, W. Richter^a, J.F. McGilp^c,
W.G. Schmidt^d, S. Wang^d, W. Lu^d, J. Bernholc^d

^aTechnische Universität Berlin, Institut für Festkörperphysik, Sekr. PN 6-1, Hardenbergstr. 36, 10623 Berlin, Germany

^bInstitut für Spektrochemie und Angewandte Spektroskopie, Albert-Einstein-Str. 9, 12489 Berlin, Germany

^cDepartment of Physics, Trinity College, Dublin 2, Ireland

^dDepartment of Physics, North Carolina State University, Raleigh, NC 27695-8202, USA

Available online 2 July 2004

Abstract

Despite much experimental and theoretical effort, the electronic and the structural properties of the $(4 \times 2)/(8 \times 2)$ -low-temperature phase of in nanowires on Si(1 1 1) are still under discussion. In our combined experimental and theoretical work we utilize the surface selectivity of reflectance anisotropy spectroscopy (RAS) to analyze the electronic (surface electronic states) properties. The RAS response is directly compared with *ab-initio* density functional theory (DFT)–local density approximation (LDA) calculations of the optical anisotropy of different surface models.

© 2004 Published by Elsevier B.V.

PACS: 73.20.–r; 73.20.At; 73.20.MF; 78.68.+m

Keywords: Indium; Silicon; Nanowire; Surface; Phase transition; Anisotropy; One dimensional; CDW; RAS; DFT–LDA; Calculation

1. Introduction

The Si(1 1 1)– (4×1) In surface has been intensively studied in the past decade, due to its unique properties [1–4]. The surface unit cell contains four indium and two silicon atoms. It features alternating indium zig-zag chains (2) separated by one silicon zig-zag chain [4,5]. The surface is quasi-one-dimensional and metallic at room temperature. The most intriguing property though is that the surface undergoes a reversible phase transition towards a (8×2) surface below

100 K [3]. This phase transition was originally explained as the formation of a charge density wave (CDW) driven by a Peierls transition [3]. This model was supported by the fact that a doubling of the surface unit cell occurs along the indium chains. Originally the (8×2) was reported to be insulating, but recent works showed only a reduction in the density of state at the Fermi level [6,7]. This as well as the observation that the positions of indium atoms change during the phase transition [8] stimulated an alternative model, where the (8×2) surface is caused by a structural change rather than an electronic one. In *first principle* calculations it was found that there are models with slight displacements of the indium atoms within the chains leading to (4×2) and (8×2) symmetries

* Corresponding author.

E-mail address: karsten.fleischer@physik.tu-berlin.de
(K. Fleischer).

which are more energetically favorable than the accepted (4×1) model [5,9]. Currently there is still some disagreement whether these models can indeed explain the low temperature phase since the surface is unstable against small contamination [10] and only complete chains undergo such a transition. Both findings are unexpected for a minimum energy structure but can be easily explained within the model of the CDW formation.

In this study we will directly compare our measurements of the optical anisotropy [11] with *first principle* calculations [9].

2. Calculation of minimum energy structure and optical anisotropy

The calculations employ a massively parallel real-space multigrid implementation [12] of the density functional theory (DFT) within the local density approximation (LDA). The Si(1 1 1)–In surface is simulated by a periodic supercell that contains 10 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. The calculated equilibrium lattice constant of 5.43 Å for silicon is used. 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.

For the room temperature (4×1) phase we studied the now commonly favored zig-zag chain model and the originally proposed π -bonded stacking fault model [2]. In order to calculate the structure of the LT phase of the Si(1 1 1)–In surface, we start from symmetry-distorted geometries with (4×2) and (8×2) translational periodicities. The resulting structures are shown in Fig. 1. For the LT phases they 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 [5], who predict a corresponding reduction from 3.87 to 3.59 Å. Also, our calculated energy differences are similar to the ones obtained by Cho et al. [5]. So we find the (8×2) structure to be 8 meV more favourable per (4×1) cell than the (4×1) reconstructed surface.

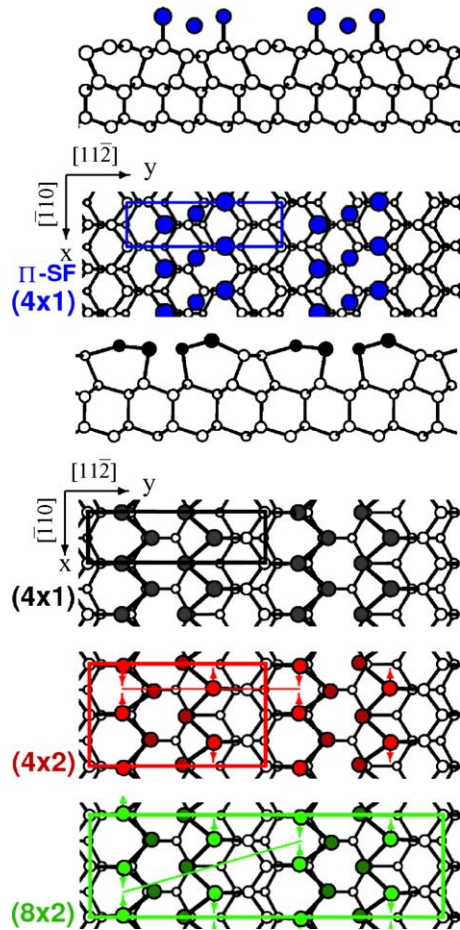


Fig. 1. Atomic positions for the calculated structures of the (4×1) π -SF and the zig-zag chain model as well as the symmetry distorted (4×2) and (8×2) models for the low temperature phase (top to bottom).

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 RAS signal is calculated out of the diagonal slab polarizability components α_{ii} and the bulk dielectric function ϵ_b following the procedure given in Refs. [13,14]. The surface dielectric function calculations were performed with uniformly distributed $\mathbf{k}$ 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. 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.

3. Experiment

For the experiment p-doped Si(1 1 1) with an off-cut angle of 4° towards the $[1\ 1\ \bar{2}]$ direction were used. Samples were heat treated at 1200°C to ensure a regular step structure of clean Si(1 1 1)– (7×7) terraces. The deposition of about 1 ML of indium at a substrate temperature of 400°C to obtain a single domain (4×1) surface was monitored with RAS. The spectra of these surfaces showed spectra similar to those of Ref. [15] and a single domain (4×1) LEED pattern was observed.

After preparation the samples were transferred in vacuum to the liquid helium cooling stage where low temperature measurements were performed. The base pressure of the system was 2×10^{-10} mbar. The RAS instrument has a spectral range from 0.8 to 6.5 eV using a CaF_2 photoelastic modulator and MgF_2 polarizers.

In order to compare the energetic positions of the anisotropy of the low temperature (8×2) phase with the room temperature (4×1) phase one has to measure both phases at the same temperatures. We therefore utilized the fact that the (8×2) surface is unstable against small contamination and therefore reverts to the (4×1) structure [10]. RAS spectra were taken for freshly prepared samples as well as for the ones kept for 1 or 3 days in vacuum. All samples had the same RAS spectra at room temperature (corresponding to the (4×1) surface). Fresh samples will show a (8×2) phase at 30 K while old ones will show a (4×1) .

In Fig. 2 we compare the calculated RAS spectra of the π -SF model of Saranin et al. with the measured anisotropy of a (4×1) surface. It can be clearly seen that this model cannot reproduce the measured lineshape and can therefore be discarded. The zig-zag chain model of the (4×1) phase in contrast describes the measured anisotropy remarkably well.

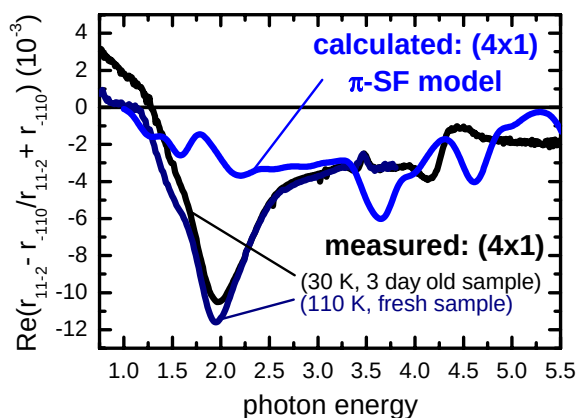


Fig. 2. RAS spectrum of the (4×1) surface compared with calculations of the π -SF model. For the measured (4×1) spectra both a fresh sample slightly above the transition temperature as well as a contaminated one below the transition temperature. The deviation from the calculation for a π -SF model is obvious.

Newly prepared samples, which undergo the phase transition towards the (8×2) phase show a doubling of the minimum structure around 2 eV into a doublet of minima centered at 1.9 and 2.2 eV (see Fig. 3). This behaviour is well described by the calculated RAS spectra corresponding to the symmetry-distorted zig-zag chain (8×2) model. Calculations based on the symmetry distorted (4×2) model show a similar effect, although the separation of the minima is not as clear as in the (8×2) case. This also compares well with the measured spectra of samples after 1 day in the UHV chamber. In such cases the phase transition is incomplete. LEED measurements only show weak “by 2” streaks and the spectra resemble a linear combination of the (4×1) and the (8×2) case. This is consistent with the STM results that only complete chains undergo the phase transition resulting in some chains in a local (4×1) order and others in the (4×2) [3]. The (8×2) symmetry cannot be seen in this case since the sample is lacking long-range order perpendicular to the chains. This is also consistent with the findings by Kumpf et al., where the (4×2) phase is described as a disordered (8×2) .

What cannot be described is the strong positive anisotropy below 1 eV, which is present for the (8×2) and (4×2) phase. Intraband transitions were not considered in the current calculation and therefore interpretation is limited to a spectral range where the optical anisotropy is dominated by interband

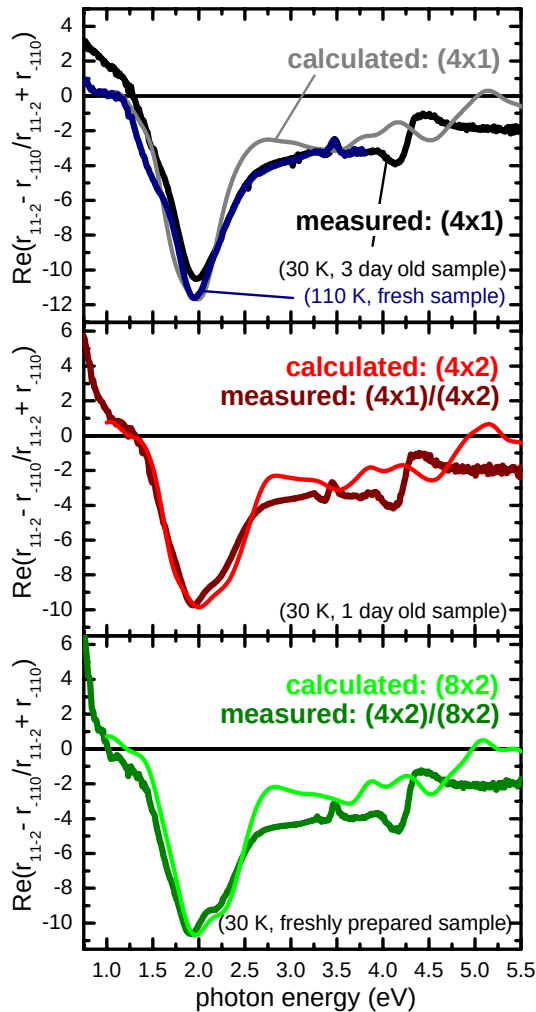


Fig. 3. RAS spectra taken at 30 K compared with calculations for the various models. The different surfaces (8×2), (4×2), (4×1) are produced by deliberate aging of the samples.

transitions. Since the calculated optical properties of the symmetry-distorted zig-zag chain model agree very well with the measured anisotropy of the low temperature phase, the underlying structural model appears to be a good description of the (8×2) phase. However, the calculation does not reveal the gap opening expected for a Peierls transition. This may be due to the omission of self-energy effects in the calculation and it appears likely that at least one of the metallic bands (labeled m_3 in Ref. [3]) will show such a gap opening, if self-energy were included. It appears,

therefore, that the competing models of the low temperature phase may both be valid. A Peierls-like instability of one metallic band, which halves the Brillouin zone, leads to a formation of a CDW. The resulting distortion of the lattice by the CDW can then explain the changes in the atomic positions (8% of the In–In distance) found in the *first principle* calculation and GIXRD measurements. Due to the presence of very low frequency In–In vibrational modes [11] and the fact that the restoring forces for displaced indium atoms are an order of magnitude smaller than those of silicon atoms at the surface [16], we think it very likely that the indium atoms will change their position on the formation of the CDW.

4. Conclusions

The distinct spectral changes in reflectance anisotropy arising from the low temperature phase transition of the Si(111)–(4×1)In surface can be reproduced by ab initio calculations of the optical properties. The spectra of the low temperature phase can be explained with the structural model described in Ref. [5], but it appears likely that aspects of this model could arise from a CDW distortion, as proposed in Refs. [3,7].

Acknowledgements

This work was supported by Enterprise Ireland Grant No. SC/2001/109/, the Irish Higher Education Authority and the SFB 290 of the Deutsche Forschungsgemeinschaft. We gratefully acknowledge grants of supercomputer time provided by the DOD Challenge Program.

References

- [1] M. Abukawa, M. Sasaki, F. Hisamatsu, T. Goto, T. Kinoshita, et al., Surf. Sci. 325 (1995) 33.
- [2] A.A. Saranin, E.A. Khrantsova, K.V. Ignatovich, V.G. Lifshits, T. Numata, et al., Phys. Rev. B: Condens. Matter 55 (1997) 5353.
- [3] H.W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, et al., Phys. Rev. Lett. 82 (1999) 4898.
- [4] O. Bunk, G. Falkenberg, J.H. Zeysing, L. Lottermoser, R.L. Johnson, et al., Phys. Rev. B 59 (1999) 12228.

- [5] J.-H. Cho, D.-H. Oh, K.S. Kim, L. Kleinman, *Phys. Rev. B* 64 (2001) 235302.
- [6] K. Sakamoto, H. Ashima, H.W. Yeom, W. Uchida, *Phys. Rev. B* 62 (2000) 9923.
- [7] H.W. Yeom, K. Horikoshi, H.M. Zhang, K. Ono, R.I.G. Uhrberg, *Phys. Rev. B* 65 (2002) 241307R.
- [8] C. Kumpf, O. Bunk, J.H. Zeysing, Y. Su, M. Nielsen, et al., *Phys. Rev. Lett.* 85 (2000) 4916.
- [9] S. Wang, W. Lu, W.G. Schmidt, J. Bernholc, *Phys. Rev. B* 68 (2003) 035329.
- [10] S.V. Ryjgov, T. Nagao, V.G. Lifehits, S. Hasegawa, *Surf. Sci.* 488 (2001) 15.
- [11] K. Fleischer, S. Chandola, N. Esser, W. Richter, J.F. McGilp, *Phys. Rev. B* 67 (2003) 235318.
- [12] E.L. Briggs, D.J. Sullivan, J. Bernholc, *Phys. Rev. B* 54 (1996) 14362.
- [13] R. DelSole, *Solid State Commun.* 37 (1981) 537.
- [14] F. Manghi, R. DelSole, A. Selloni, E. Molinari, *Phys. Rev. B* 41 (1990) 537.
- [15] F. Pedreschi, J.D. O'Mahony, P. Weightman, J.R. Power, *Appl. Phys. Lett.* 73 (1998) 2152.
- [16] F. Bechstedt, A. Krivosheeva, J. Furthmüller, A. Stekolnikov, *Phys. Rev. B* 68 (2003) 193406.