
Si(111)-In Nanowire Optical Response from Large-scale Ab Initio Calculations

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Summary. The anisotropic optical response of Si(111)-(4×1)/(8×2)-In in the mid-infrared, where significant changes in the band structure between competing models of this important quasi-1D system are expected, has been calculated from *first principles*. Two characteristic peaks are calculated for the hexagon model of the (8×2) structure, but not for the trimer model. The comparison with recent infrared reflection anisotropy spectroscopy (RAS) data—showing the replacement of the anisotropic Drude tail of the (4×1) phase by two peaks at 0.50 eV and 0.72 eV—gives strong evidence for the hexagon model. Our calculations thus settle decades of intense debate about the ground-state geometry of this important prototype for quasi one-dimensional electronic systems.

1 Introduction

One-dimensional (1D) electronic systems are attracting considerable interest for both fundamental and technological reasons. Fascinating phenomena, such as spin-charge separation [1], and charge-density wave (CDW) formation due the Peierls instability may appear, while quasi-1D structures are being investigated as atomic-scale interconnects in devices. Such structures can be grown by self-assembly on Si surfaces [2], where the existence of an energy gap prevents the coupling of the electronic states of the nanostructure with the substrate in the vicinity of the Fermi level, thus preserving the quasi-1D character of the nanostructure states.

An intensively studied model system is 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). Results from many different experiments, as well as *ab initio* band structure calculations, agree that the structure is metallic, with the In atoms forming two parallel zigzag chains, which are separated by zigzag Si chains that resemble the π -bonded chains of Si(111)-(2×1) [3–14]. The structure has three quasi-1D surface state bands, which disperse strongly and cross the Fermi level along

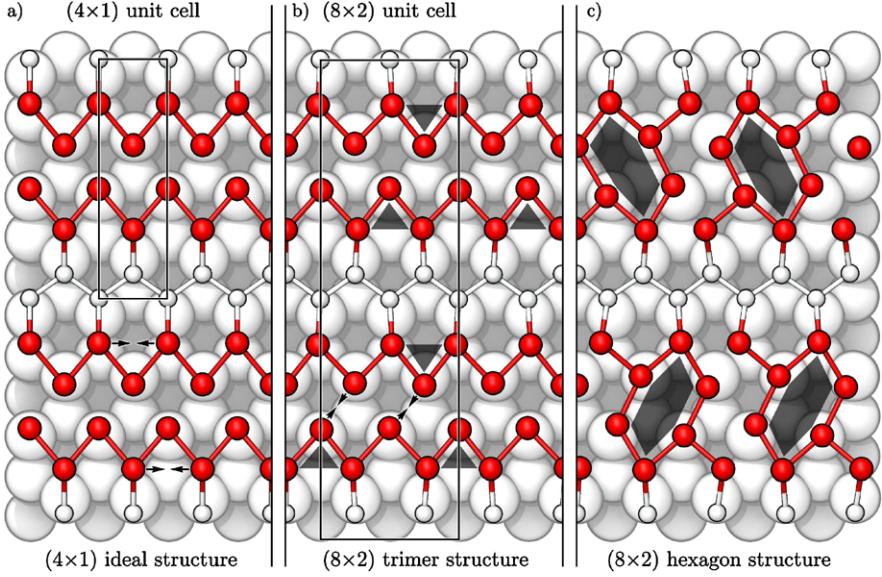


Fig. 1. Schematic top views of the room temperature Si(111)- (4×1) -In phase (a) and the trimer (b) hexagon models (c) proposed to describe the low-temperature structure of the Si(111)-In nanowire array. Red and grey balls indicate In and Si atoms, respectively

the chain direction, and show only a weak dispersion perpendicular to the chain.

Yeom et al. [15] 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 energy. From photoemission and scanning tunnelling microscopy (STM) studies they concluded that this phase formed a 1D CDW system driven by a Peierls instability. These intriguing results provoked much experimental and theoretical work. However, the origin of the phase transition remains controversial. The phase transition cannot be based on a simple CDW model because only one of the metallic bands nests properly [3, 15–19]. A triple-band Peierls instability has been suggested, where an interband charge transfer modifies the Fermi surface to improve nesting [17], while a periodic lattice distortion that lowers the energy has also been suggested [6, 9, 10, 20]. Recently, it has been proposed that, while the Peierls transition is important, other structural transitions are cooperatively involved [21].

Not only the mechanism of the $(4 \times 1) \rightarrow (8 \times 2)$ phase transition, but also the LT ground-state and its properties remain controversial. While the RT (4×1) phase is a quasi-1D metal [12, 16, 22], it has been variously suggested that the LT (8×2) phase is metallic, but with a lower density of states at the Fermi level [19, 20, 23], semimetallic [19], and semiconducting with a fun-

damental energy gap of 0.1–0.3 eV [15–18, 21]. Most *ab initio* calculations predict the nanowire ground state to be characterized by the formation of In trimers (cf. Fig. 1b) and find no gap opening [6, 7, 9, 10]. Recently, however, a structure with In hexagons, resulting from shear distortions in neighbouring chains (Fig. 1), has been predicted, which is semiconducting [24]. In Ref. [24] it was argued that the metallic RT phase arises from dynamic fluctuations between degenerate ground states, but recent photoemission [21] and Raman spectroscopy [11] results have cast doubt on this model. Total-energy calculations [13] of the hexagon and the trimer model for the LT phase concluded that an unambiguous identification of the internal structure of the ground state on energetic arguments is problematic. The energy differences between the competing structures are very small and 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 [25] state that the hexagon model is not stable, but the model has been supported recently by positron diffraction studies [26].

Very recently, optical spectroscopic information from a new spectral region has become available. Optical excitations around the Fermi level, in the mid-IR spectral range from 0.31 eV to 0.99 eV were probed with infrared spectroscopic ellipsometry (IRSE) and reflection anisotropy spectroscopy (RAS) [27]. As we will show in the following, the comparison of the measured data with spectra calculated from *first principles* provides strong evidence that excludes the trimer model and supports the hexagon model of the In nanowire ground state.

2 Computational Method

The theoretical data are obtained using density functional theory (DFT) within the local density approximation (LDA) for exchange and correlation as implemented in VASP [28]. Within the DFT calculations, the system of Kohn-Sham equations

$$\left\{ -\frac{\hbar^2}{2m} \Delta + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \right\} \psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} \psi_{n\mathbf{k}} \quad (1)$$

$$n(\mathbf{r}) = \sum_{n,\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}|^2 \quad (2)$$

is solved iteratively for the external potential $V_{ext}(\mathbf{r})$ until self-consistency in the total electron density $n(\mathbf{r})$ is reached. Plane waves serve as basis set for the Kohn-Sham orbitals $\psi_{n\mathbf{k}}(\mathbf{r})$. The ground-state DFT calculations were parallelized for different bands and sampling points in the Brillouin zone using the message passing interface (MPI). Parallelization over bands and plane wave coefficients at the same time reduces the communication overhead significantly.

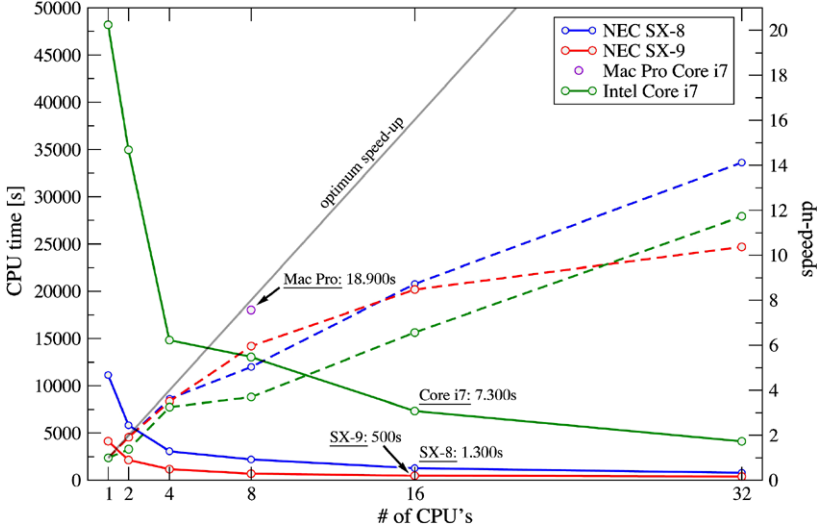


Fig. 2. Wall clock time and speedup for DFT calculations for the hexagon model of the Si(111)-In nanowire array containing around 200 atoms. The calculations were performed with the Stuttgart optimized VASP version on the HLRS NEC SX-8 and SX-9 machines. In comparison, we show data for a local Linux cluster (Intel Core i7, 24 Twin-nodes with 4 CPU's 2.5 GHz Quad Core Xeon each) and Mac Pro workstations (Intel Core i7)

Figure 2 shows benchmark calculations to determine the electronic ground state of the 200 atom cell used for surface modeling in our project. The calculations within this project were performed on the NEC SX-8 and SX-9 of the Höchstleistungs-Rechenzentrum Stuttgart. As can be seen, a reasonable scaling is achieved for using up to 32 CPUs.

Reflection anisotropy spectroscopy (RAS) is a non-destructive optical probe of surfaces that is capable of operation within a wide range of environments [29–31]. For a long time, however, a lack of adequate theoretical treatments presented a substantial barrier to the understanding and full exploitation of RAS spectra. This situation changed at the end of the nineties, when powerful computers allowed for the realistic modelling of the surface optical response from *first principles* [32–34]. This computational progress could build on substantial earlier efforts to understand the light-surface interaction, see, e.g., Refs. [35, 36]. Del Sole obtained an expression for the surface contribution [37] to the reflectance, $\Delta R/R$, where R is the reflectance according to the Fresnel equation. For s -light polarized along i and normal incidence it holds

$$\frac{\Delta R_i}{R}(\omega) = \frac{4\omega}{c} \Im \left\{ \frac{\Delta \epsilon_{ii}(\omega)}{\epsilon_b(\omega) - 1} \right\}, \quad (3)$$

where ϵ_b is the bulk dielectric function, and

$$\begin{aligned} \Delta\epsilon_{ij} = & \int dzdz' [\epsilon_{ij}(\omega; z, z') - \delta_{ij}\delta(z - z')\epsilon_0(\omega; z)] \\ & - \int dzdz'dz''dz''' \epsilon_{iz}(\omega; z, z') \epsilon_{zz}^{-1}(\omega; z', z'') \epsilon_{zj}(\omega; z'', z'''). \end{aligned} \quad (4)$$

Here $\epsilon_{ij}(\omega; z, z')$ is the non-local *macroscopic* dielectric tensor of the solid-vacuum interface accounting for all many-body and local-field effects [38]. (4) can be evaluated by replacing the semi-infinite crystal by an artificial super-cell, large enough to represent the vacuum as well as the surface and bulk regions of the crystal under investigation. Provided that (i) the material slab is large enough to properly describe the surface region of the crystal, i.e., the surface as well as surface-modified bulk wave-functions and (ii) the off-diagonal terms of the dielectric tensor are small compared to the diagonal ones, a simple expression for the surface contribution to the reflectivity can be derived [39]

$$\frac{\Delta R_i}{R}(\omega) = \frac{4\omega}{c} \Im \left\{ \frac{\alpha_{ii}^{hs}(\omega)}{\epsilon_b(\omega) - 1} \right\}. \quad (5)$$

Here $\alpha_{ii}(\omega)$ with $i = x, y$ is the diagonal tensor component of the slab polarizability.

Here we calculate $\alpha_{ij}(\omega)$ in the independent-particle approximation from the Kohn-Sham conduction/valence orbitals $|\mathbf{c}\mathbf{k}\rangle/|\mathbf{v}\mathbf{k}\rangle$ and eigenvalues $\epsilon_{c/k}$

$$\alpha_{ij}(\omega) = \frac{4e^2\hbar^2}{\Omega} \sum_{\mathbf{k}} \sum_{c,v} \frac{\langle \mathbf{c}\mathbf{k} | v_i | \mathbf{v}\mathbf{k} \rangle \langle \mathbf{v}\mathbf{k} | v_j | \mathbf{c}\mathbf{k} \rangle}{[\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})] \left([\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})]^2 - \hbar^2 [\omega + i\eta]^2 \right)}, \quad (6)$$

where v_i denotes the velocity operator. The calculation of the polarizability tensor for the structure shown in Fig. 1 typically requires 96 GB memory and 21 hours wall clock time using 16 CPU's of the SX-8.

3 Results

Figure 3 shows measured and calculated RAS spectra for the In nanowire array. The measured data reveal a smooth increase to low energy for the RT (4×1) phase, while the LT (8×2) phase shows two sharp positive peaks at 0.50 eV and 0.72 eV. 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 metal-insulator transition [7, 40, 41].

The calculated anisotropy of both the trimer and hexagon models of the (8×2) structure agree well with the experiment above 0.7 eV, as has been reported previously [41]. Below 0.7 eV, only the hexagon model looks similar to the experimental results. In particular, two positive peaks are predicted,

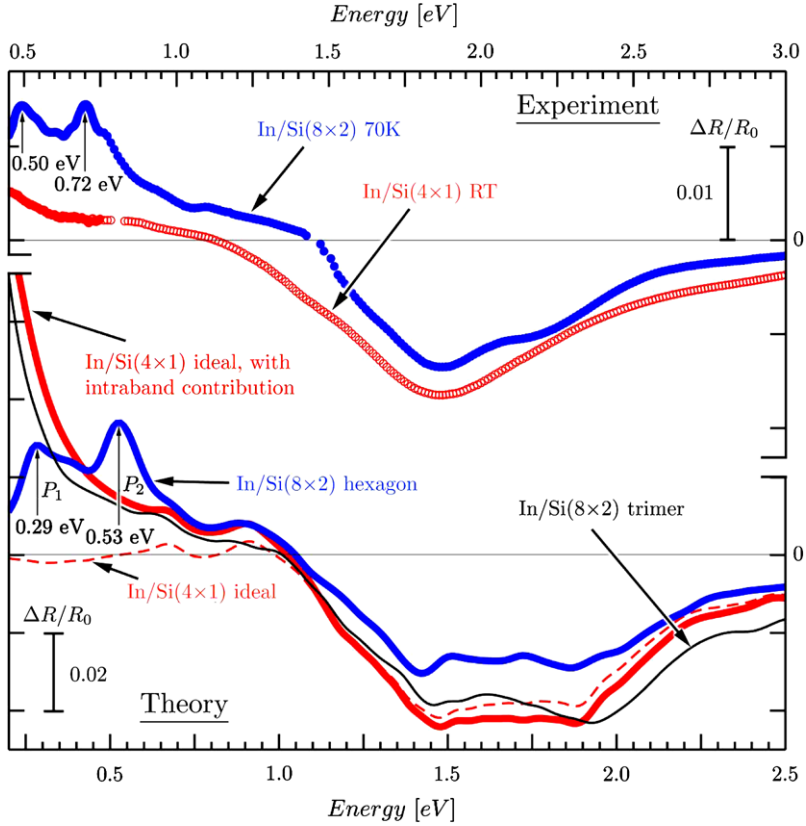


Fig. 3. RAS spectra of Si(111)-(4×1)-In at RT (300 K) and Si(111)-(8×2)-In at LT (70 K): upper, experiment; lower, theory. Note the different scales

separated by 0.24 eV. This splitting agrees very well with the experimental splitting of 0.22 eV. The origin of the two peaks in the mid IR can be traced to optical transitions close to the M point of the surface Brillouin zone, indicated by P_1 and P_2/P'_2 in Fig. 4. Around M , nearly parallel valence and conduction bands close to the Fermi level give rise to a high joint density of states. From the orbital character of states (not shown here) we can assign P_1 to transitions between bonding and non-bonding In chain states within the single In zigzag chains, while P_2 and P'_2 involve in addition In-In bonds between the two parallel zigzag chains. These bonds are exclusively formed for the hexagon model (Fig. 1). The spectra measured in the mid-IR are thus directly related to the hexagon structure of the In nanowire array.

In addition to the optical transitions in the region of the $\overline{XM}$ high-symmetry line we observe significant contributions to the optical anisotropy from transitions within the Brillouin zone. To visualize these transitions a 3-dimensional representation of the surface Brillouin zone is shown in Fig. 5.

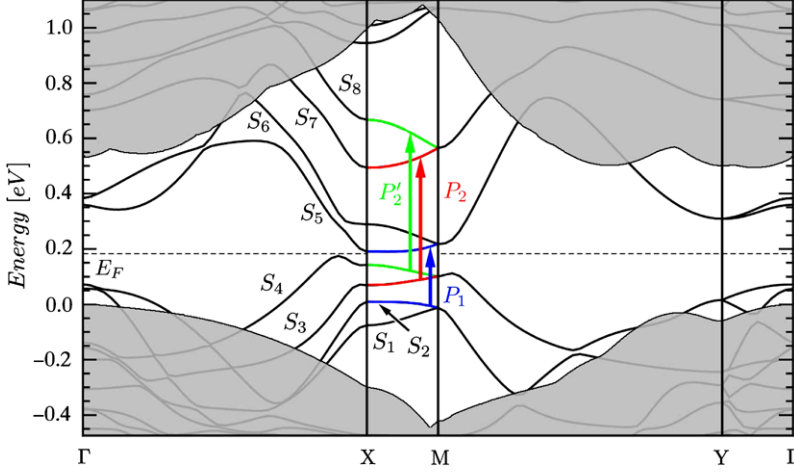


Fig. 4. Band structure of the hexagon model for Si(111)-(8 $\times$ 2)-In calculated within DFT-LDA. Pronounced optical transitions showing up in the RAS spectra are marked. Gray regions correspond to the projected Si bulk bands. The bulk valence band maximum is chosen as energy zero. The Fermi level is indicated

The notation of the surface bands $S_1 - S_8$ and the peaks $P_1, P_2/P'_2$ refers to Figs. 4 and 3, respectively. The transitions indicated in Fig. 5b, c take place over the whole width of the Brillouin zone, while the transitions in Fig. 5d, e occur either near the $\overline{\Gamma X}$ or $\overline{MY}$ high-symmetry lines only. In some cases transitions from and to the same bands contribute to different peaks: 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.

Detailed comparison of the simulated spectra with the measured data reveals that the calculated mid-IR peaks are redshifted by 0.25 eV (note the different scales in Fig. 3). The underestimation of excitation energies is typical for DFT calculations where self-energy effects are neglected. 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 [42]. 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 [13]. A larger shift of 0.5 eV, typical for Si excitation energies [42], applies to the higher energy negative optical anisotropies, because the optical transitions involve Si states [41]. Allowing for these energy shifts, the agreement between the calculated and measured RAS spectra is truly impressive.

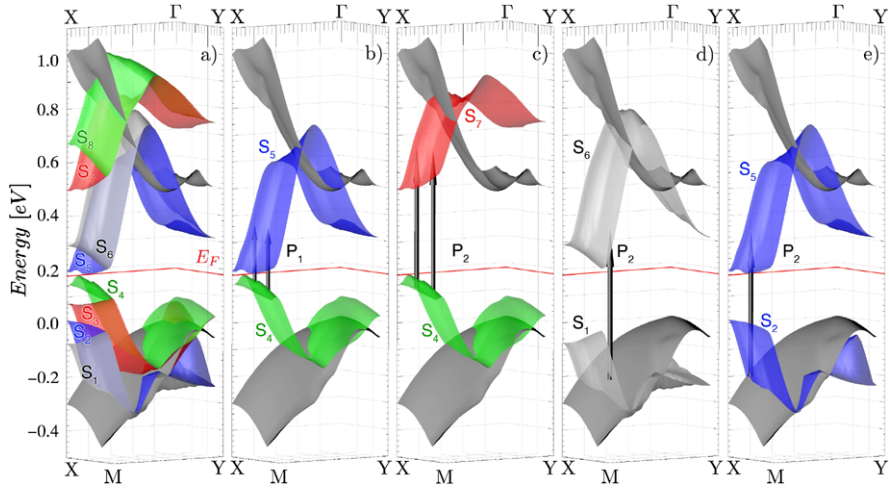


Fig. 5. a 3-D band structure of the hexagon model for Si(111)-(8 $\times$ 2)-In calculated within DFT-LDA. The notation of bands is consistent with Fig. 4. Pronounced optical transitions from *within* the Brillouin zone causing the peaks P_1 and P_2 in the RAS spectra are shown in **b** and **c–e**, respectively. The Fermi level is indicated by E_F

4 Summary

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 $\times$ 1)-In phase formed by zig-zag chains of In atoms at room temperature and a semiconducting (8 $\times$ 2) phase characterized by In atoms forming hexagons. The present computational results in conjunction with recent experimental data are likely to settle an intense debate on the ground-state geometry of one of the arguably most important model systems for quasi-1D metallic nanowires.

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References

1. Elliott H. Lieb and F.Y. Wu, Phys. Rev. Lett. **20**, 1445 (1968).
2. F.J. Himpsel, K.N. Altman, R. Bennewitz, J.N. Crain, A. Kirakosian, J.L. Lin, and J.L. McChesney, J. Phys.: Condens. Matter **13**, 11097 (2001).
3. T. Abukawa, M. Sasaki, F. Hisamatsu, T. Goto, T. Kinoshita, A. Kakizaki, and S. Kono, Surf. Sci. **325**, 33 (1995).

4. I.G. Hill and A.B. McLean, Phys. Rev. Lett. **82**, 2155 (1999).
5. O. Bunk, G. Falkenberg, J.H. Zeysing, L. Lottermoser, R.L. Johnson, M. Nielsen, F. Berg-Rasmussen, J. Baker, and R. Feidenhans'l, Phys. Rev. B **59**, 12228 (1999).
6. J.-H. Cho, D.-H. Oh, K.S. Kim, and L. Kleinman, Phys. Rev. B **64**, 235302 (2001).
7. S. Wang, W. Lu, W.G. Schmidt, and J. Bernholc, Phys. Rev. B **68**, 035329 (2003).
8. K. Fleischer, S. Chandola, N. Esser, W. Richter, and J.F. McGilp, Phys. Rev. B **67**, 235318 (2003).
9. J.-H. Cho, J.-Y. Lee, and L. Kleinman, Phys. Rev. B **71**, 081310(R) (2005).
10. X. Lopez-Lozano, A. Krivosheeva, A.A. Stekolnikov, L. Meza-Montes, C. Noguez, J. Furthmüller, and F. Bechstedt, Phys. Rev. B **73**, 035430 (2006).
11. K. Fleischer, S. Chandola, N. Esser, W. Richter, and J.F. McGilp, Phys. Rev. B **76**, 205406 (2007).
12. T. Kanagawa, R. Hobara, I. Matsuda, T. Tanikawa, A. Natori, and S. Hasegawa, Phys. Rev. Lett. **91**, 036805 (2003).
13. A.A. Stekolnikov, K. Seino, F. Bechstedt, S. Wippermann, W.G. Schmidt, A. Calzolari, and M. Buongiorno Nardelli, Phys. Rev. Lett. **98**, 026105 (2007).
14. S. Wippermann, N. Koch, and W.G. Schmidt, Phys. Rev. Lett. **100**, 106802 (2008).
15. H.W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, J. Schaefer, C.M. Lee, S.D. Kevan, T. Ohta, T. Nagao, and S. Hasegawa, Phys. Rev. Lett. **82**, 4898 (1999).
16. T. Tanikawa, I. Matsuda, T. Kanagawa, and S. Hasegawa, Phys. Rev. Lett. **93**, 016801 (2004).
17. J.R. Ahn, J.H. Byun, H. Koh, E. Rotenberg, S.D. Kevan, and H.W. Yeom, Phys. Rev. Lett. **93**, 106401 (2004).
18. S.J. Park, H.W. Yeom, S.H. Min, D.H. Park, and I.W. Lyo, Phys. Rev. Lett. **93**, 106402 (2004).
19. J. Guo, G. Lee, and E.W. Plummer, Phys. Rev. Lett. **95**, 046102 (2005).
20. K. Sakamoto, H. Ashima, H.W. Yeom, and W. Uchida, Phys. Rev. B **62**, 9923 (2000).
21. Y.J. Sun, S. Agario, S. Souma, K. Sugawara, Y. Tago, T. Sato, and T. Takahashi, Phys. Rev. B **77**, 125115 (2008).
22. T. Uchihashi and U. Ramsperger, Appl. Phys. Lett. **80**, 4169 (2002).
23. H.W. Yeom, K. Horikoshi, H.M. Zhang, K. Ono, and R.I.G. Uhrberg, Phys. Rev. B **65**, 241307(R) (2002).
24. C. Gonzalez, F. Flores, and J. Ortega, Phys. Rev. Lett. **96**, 136101 (2006).
25. Jun-Hyung Cho and Jung-Yup Lee, Phys. Rev. B **76**, 033405 (2007).
26. Y. Fukaya, M. Hashimoto, A. Kawasuso, and A. Ichimiya, Surf. Sci. **602**, 2448 (2008).
27. S. Chandola, K. Hinrichs, M. Gensch, N. Esser, S. Wippermann, W.G. Schmidt, F. Bechstedt, K. Fleischer, and J.F. McGilp, Phys. Rev. Lett. **102**, 226805 (2009).
28. G. Kresse and J. Furthmüller, Comp. Mat. Sci. **6**, 15 (1996).
29. W. Richter, Philos. T. Roy. Soc. A **344**, 453 (1993).
30. D.E. Aspnes, Solid State Commun. **101**, 85 (1997).

31. P. Weightman, D.S. Martin, R.J. Cole, and T. Farrel, Rep. Prog. Phys. **68**, 1251 (2005).
32. W.G. Schmidt, F. Bechstedt, and J. Bernholc, J. Vac. Sci. Technol. B **18**, 2215 (2000).
33. W.G. Schmidt, K. Seino, P.H. Hahn, F. Bechstedt, W. Lu, S. Wang, and J. Bernholc, Thin Solid Films **455/456**, 764 (2004).
34. W.G. Schmidt, F. Fuchs, A. Hermann, K. Seino, F. Bechstedt, R. Paßmann, M. Wahl, M. Gensch, K. Hinrichs, N. Esser, S. Wang, W. Lu, and J. Bernholc, J. Phys.: Condens. Matter **16**, S4323 (2004).
35. J.D.E. McIntyre and D.E. Aspnes, Surf. Sci. **24**, 417 (1971).
36. A. Bagchi, R.G. Barrera, and A.K. Rajagopal, Phys. Rev. B **20**, 4824 (1979).
37. R. Del Sole, Solid State Commun. **37**, 537 (1981).
38. R. Del Sole and E. Fiorino, Phys. Rev. B **29**, 4631 (1984).
39. F. Manghi, R. Del Sole, A. Selloni, and E. Molinari, Phys. Rev. B **41**, 9935 (1990).
40. K. Fleischer, S. Chandola, Norbert Esser, W. Richter, J.F. Mcgilp, W.G. Schmidt, S. Wang, W. Lu, and J. Bernholc, Appl. Surf. Sci. **234**, 302 (2004).
41. S. Wippermann and W.G. Schmidt, Surf. Sci. **603**, 247 (2009).
42. P.H. Hahn, W.G. Schmidt, and F. Bechstedt, Phys. Rev. Lett. **88**, 016402 (2001).