Adatom-Induced Conductance Modification of In Nanowires: Potential-Well Scattering and Structural Effects

S. Wippermann, N. Koch, and W. G. Schmidt

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

(Received 14 August 2007; revised manuscript received 5 February 2008; published 11 March 2008)

First-principles calculations on the influence of adatoms (In, Pb, H, O) on the Landauer conductance of Si substrate-supported atomic-scale In nanowires are performed. Despite the increase of the total (and partially even local) density of states at the Fermi level due to the adsorption, all adatom species lower the nanowire conductance. Apart from hydrogen, which barely changes the transport properties, the conductance drop is pronounced, ranging from 17% for Pb to 38% for In. It is related to potential-well scattering and/or structural deformations of the nanowires.

DOI: 10.1103/PhysRevLett.100.106802 PACS numbers: 73.63.−b, 68.43.Bc, 73.20.At

The atom-by-atom fabrication and modification of low-dimensional nanostructures is one of the impressive technological advances of recent years. It allows for the manipulation and positioning of single atoms or molecules in nanodevices such as artificial atomic-scale wires; see, e.g., Ref. [1]. Such quasi-one-dimensional (1D) structures do not only show fascinating physical properties, but they also have a large technological potential, e.g., as atomic-scale interconnects. Therefore there is an increasing interest in understanding and predicting the electronic properties of quasi-1D systems [2,3]. Highly anisotropic surface superstructures have attracted considerable attention in this context.

The ordered array of In "nanowires" formed on Si(111) 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 for its RT phase (see Fig. 1 for a top view) that is well accepted [4–12]: Each nanowire consists of two zigzag chains of In atoms within a (4×1) surface periodicity. There are still many open questions, concerning, e.g., the temperature-induced $(4 \times 1) \rightarrow (8 \times 2)$ phase transition of the In overlayer structure [13–16], the modification of its structural and electronic properties upon adsorption of foreign as well as In adatoms [17–19], and the electron transport properties of ideal and defective In nanowires [16,20–22]. It was found that the conductivity of the—at RT metallic [20,21]—In nanowires is roughly halved by adsorbing additional In (0.1 ML) on top of the wires [22]. The mechanism that quenches the conductance, and the influence of other species on the wire resistance is not known, however, and will be investigated here.

In the present study, we use first-principles electron transport calculations to investigate the impact of different adatoms (In, Pb, O, H) on the nanowire conductance. The calculations reproduce the distinct reduction measured for In adatoms and predict pronounced drops for Pb and O as well. The mechanisms, however, are different. While mainly potential-well scattering occurs for Pb, the local distortion of the wire geometry reduces the conductance for In. Both effects show up for oxidized wires.

Our calculations are based on the plane-wave pseudopotential PWSCF implementation [23] of density functional theory (DFT) within the local density approximation (LDA). DFT calculations have difficulty to describe accurately the subtle energetics of the temperature-induced $(4 \times 1) \rightarrow (8 \times 2)$ nanowire phase transition [15,16]. On the other hand, all measured properties of the RT (4×1) phase are well reproduced within DFT [7,8,10,12]. Therefore, and because the potential energy surfaces (PES) of the adatoms considered here (see Fig. 1) turn out to be highly corrugated, we expect DFT calculations to be adequate for ideal and adatom perturbed In/Si(111)-(4×1) surfaces. In detail, we use a $8 \times 2 \times 1$ **k**-point mesh to sample the Brillouin zone and an energy cutoff of 400 eV for the wave-function expansion. The In

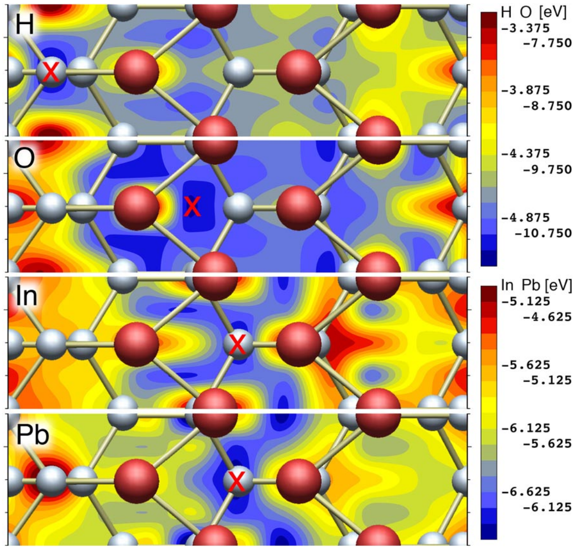

FIG. 1 (color online). Potential energy surface calculated for H, O, In, and Pb adatoms on the In/Si(111)-(4×1) surface. Large and small balls indicate In and Si atoms, respectively. The minimum energy positions for the adsorbed species are marked.

4d states are treated as core electrons. Otherwise, our approach equals the one in Ref. [16]. This holds also for the electron transport calculation: The Landauer conductance in the limit of zero bias is computed using the WanT approach [24], i.e., a Green function formalism based on "maximally localized Wannier functions" [25] as a minimal basis set. Thereby we exploit the fact that the In-related surface states close to the Fermi energy (E_F) depend very little on the substrate [26] and study 1D model structures that contain only the In and nearest neighbor Si atoms with the remaining Si dangling bonds terminated with hydrogen. Test calculations for structures with one and two Si bilayers [27] confirm the validity of this approach. For the transport calculations a $16 \times 1 \times 1$ $\mathbf{k}$-point mesh and an energy cutoff of 250 eV are found to lead to converged spectra.

We start by determining the PES for H, O, In, and Pb adsorbed on the nanowire array. These calculations are performed in a (4×3) unit cell with three bilayers of Si. The calculated energy landscapes are shown in Fig. 1. In and Pb prefer a position between neighboring In chains, O adsorbs threefold coordinated on top of the In chain and H bonds to a surface silicon atom. While the lateral positions of In and Pb adatoms are nearly equal, the adsorption geometry is not. The In adatom is located almost in-plane with the In chain atoms, whereas Pb prefers a pyramidal configuration, see Fig. 2. This affects also the structural relaxation of the In nanowire. Comparatively small deformations occur for Pb, but large atomic shifts are found for In deposition. This is reflected in the standard deviations of the In-In bond length distribution and the average atomic shifts compiled in Table I.

Starting from the relaxed adatom positions, the influence of the perturbation on the In nanowire conductance is calculated by using a lead-conductor-lead partitioning of the system. Here the In chain segment with the adatom forms the conductor [within a (8×8) wire segment] and the semi-infinite leads are modeled with ideal In nanowires. The calculated conductance spectra of the ideal and adatom perturbed In nanowires are shown in Fig. 3. The transmittance at E_F calculated for the unperturbed nanowire somewhat overestimates—by roughly a factor of 2—the experimentally determined surface state conductance in the RT regime [20–22]. This can be attributed to the effect of the contacts and their scattering as well as to the thermal dissipative scattering due to phonons at finite temperature. These effects arise as well for perturbed In nanowires. However, the phonon scattering—neglected here—will modify the electron transport to different degrees [28].

Compared to the calculations for the ideal structure, a reduction of the quantum conductance at E_F by more than one third compared to the ideal chain is calculated for the case of In adatoms. While the experimental conditions are not sufficiently well defined to allow for a quantitative comparison, the calculated reduction is of the same order as measured [22]. Interestingly, apart from hydrogen which does not substantially modify the electron transport properties, the calculations predict distinct conductance drops as well for Pb and, in particular, for O, see Table I. One might want to explain this finding with a reduced density of electronic states (DOS) at E_F. However, as shown in Fig. 3 and Table I, (i) the DOS increases irrespective of the specific adatom deposited and (ii) the DOS of the perturbed nanowires shows at best a very weak correlation with the conductance. For example, the DOS at E_F is nearly equal for Pb and O. However, O is far more effective in reducing the conductance. Obviously, the DOS does not suffice to understand the trend of the conductance change.

This holds also for the local density of states (LDOS) at E_F. In all cases we find a distinct and adatom-specific LDOS modification upon adsorption, see Fig. 4. For example, In causes a sharp local DOS increase close to the adatom that is accompanied by a DOS depletion at the next nearest neighbor distance. The adsorption of O leads to a DOS redistribution from the neighboring to the adatom decorated In chain. Even hydrogen—that does not affect the nanowire conductance and adsorbs on Si atoms rather than on the In chain—clearly affects the nanowire LDOS. Thus, neither the total nor the local DOS seem very helpful for understanding the influence of adatoms on the nanowire conductance.

In the case of CO adsorption on substrate-supported Au chains, the drastic conductance drop could be traced to the deep potential well arising at the adsorption site [3]. In order to see if a similar mechanism acts here, we extract the local effective potential from our DFT calculations. This

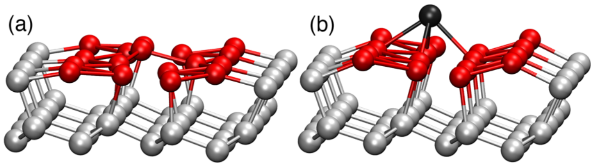

FIG. 2 (color online). Side views of (a) In and (b) Pb adatoms adsorbed on the In/Si(111)-(4×1) surface.

TABLE I. Standard deviation σ of the In-In bond length distribution and average shift $\bar{\Delta}$ of the In chain atoms for ideal and defect-modified nanowires. Average quantum conductance G in the energy interval ± 0.05 eV around E_F, G' refers to the respective adatom structure without the adatom. The last column contains the electronic density of states at E_F.

Adatom	σ(Å)	$\bar{\Delta}$(Å)	$G(\frac{2e^2}{h})$	$G'(\frac{2e^2}{h})$	DOS (a.u.)
Ideal	0.01	0.00	3.75	3.75	0.70
In	0.12	0.38	2.31	2.77	0.95
Pb	0.07	0.16	3.11	3.72	1.23
H	0.04	0.21	3.60	3.74	1.44
O	0.11	0.24	2.43	3.25	1.22

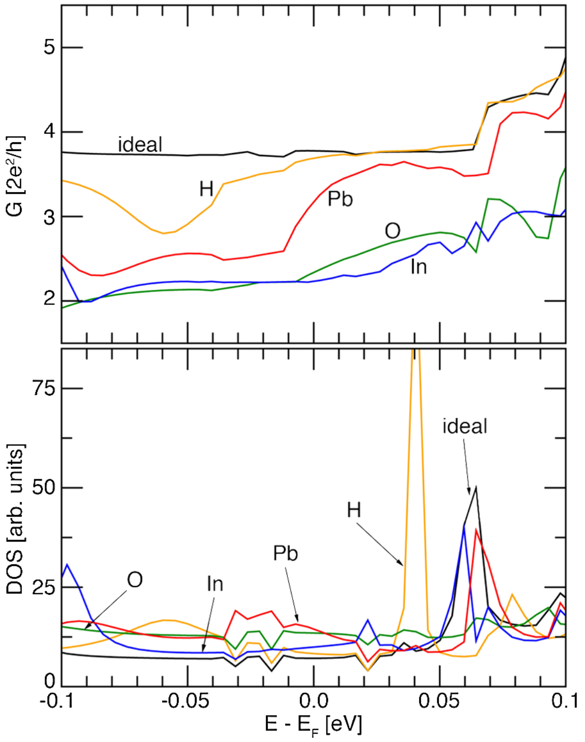

FIG. 3 (color online). Quantum conductance spectrum for electron transport along the wire direction (upper part) and total density of states (lower part) calculated for ideal and adatom-modified In/Si(111) structures.

potential is then averaged in a plane perpendicular to the nanowire direction chosen large enough to contain—within their covalent radii—the nanowire In atoms as well as the adatoms. As shown in Fig. 5, the systems studied here differ drastically with respect to the local potential. A very deep potential well is formed upon Pb adsorption, while additional In atoms barely change the potential along the wire direction. Thus it seems likely that the conductance modification upon Pb adsorption obeys a similar mechanism as proposed for CO adsorbed on Au chains [3]. Judging from Fig. 5, however, this mechanism cannot explain the conductance drop upon In deposition: In adatoms reduce the In nanowire transmittance even more than Pb, but do not give rise to large potential fluctuations. These considerations are corroborated by 1D model calculations, where we solve the time-dependent Schrödinger equation for the potentials shown in Fig. 5. The transmission of Fermi wave-vector electrons across the Pb potential well is reduced by 8%, while we obtain a reduction by only 3% in case of In.

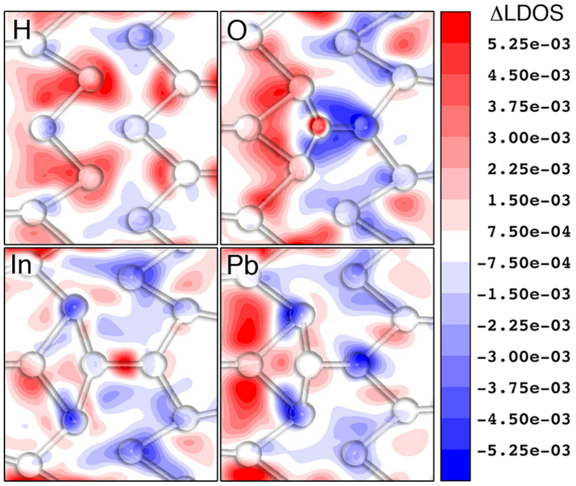

FIG. 4 (color online). Adsorption induced changes (in a.u.) of the local density of states at E_F projected on the plane of the Si(111) surface. Negative and positive values indicate local DOS depletion and accumulation with respect to the ideal In/Si(111) system, respectively.

In order to understand the conductance drop in the latter case, we come back to our initial observation that the adatoms deform the nanowire to different degrees, as can be seen from Table I and Figs. 2 and 4. While the smallest deformations are observed for H and Pb adsorption, In causes substantial strain. Oxygen represents an intermediate case.

The computational modeling allows for separating the impact of the adatom-induced structure deformation from the impact of the adatom itself: We perform transport calculations for nanowire structures that are deformed according to their relaxation in response to the adatom, but do not contain the adatom. The results are shown in Fig. 6 and compiled in Table I. As can be seen here, the—comparatively small—geometry changes of the In nanowire upon adsorption of hydrogen or lead do not substantially reduce the wire conductance. This is in contrast to the stronger distortions caused by the adsorption of oxygen or indium, where moderate to strong conductance reductions are calculated.

This does now allow for a classification of the adatom-induced conductance modifications. Pb adsorption does not substantially modify the nanowire geometry, but forms a deep potential well that effectively scatters the electrons and thus reduces the transmittance. No significant

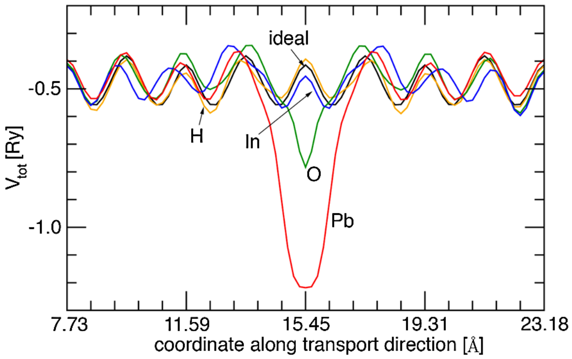

FIG. 5 (color online). Averaged (see text) effective potential along the wire direction calculated for ideal and adatom-modified In/Si(111) structures.

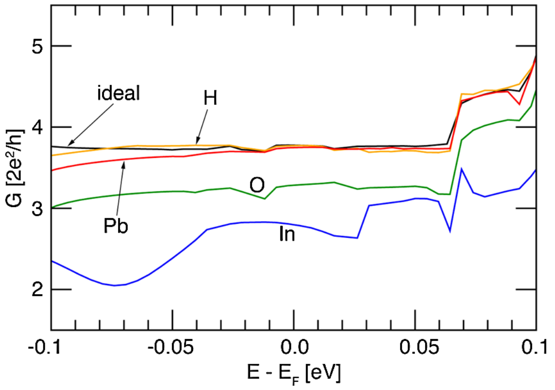

FIG. 6 (color online). Quantum conductance spectrum for electron transport along the wire direction calculated for ideal and adatom-modified In/Si(111) structures that do, however, not contain the adatom.

potential well forms for In. Here the conductance drop is related to the wire deformation. Both factors contribute in the case of oxygen. A moderate potential well is formed and on top of that the nanowire gets somewhat deformed. This results in a conductance drop of similar magnitude as calculated for In. Hydrogen, finally, does neither act as a potential well nor does it strain significantly the nanowire. Consequently, it has no substantial impact on the electron transport.

To conclude, the In nanowire array on Si(111)—intensively studied by many researchers—is a very interesting test bed also for conductance modification at the atomic scale: It is well accessible to both experiment and first-principles theory and thus helps to gain a deeper understanding of nanoscale electron transport. The first-principles calculations performed here for ideal and adatom deposited In nanowires predict an adatom-specific and in some cases very pronounced decrease of the wire conductivity upon adatom deposition. For In adatoms, where measurements exist, the reduction by more than one third agrees with the existing data. For oxygen deposition, the calculations predict a similar drop in conductance, whereas the impact of Pb atoms is slightly smaller. The adsorption of hydrogen does not substantially reduce the conductance. The nanowire conductance modification due to the adatoms can be related to different mechanisms: potential-well scattering (Pb), nanowire deformation (In), or a combination of both effects (O).

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft as well as supercomputer time provided by the HLRS Stuttgart and the Paderborn PC^2.

[1] N. Nilius, T. M. Wallis, and W. Ho, Science **297**, 1853 (2002); G. V. Nazin, X. H. Qiu, and W. Ho, Science **302**, 77 (2003).
[2] N. Nilius, T. M. Wallis, and W. Ho, Phys. Rev. Lett. **90**, 186102 (2003).
[3] A. Calzolari, C. Cavazzoni, and M. Buongiorno Nardelli, Phys. Rev. Lett. **93**, 096404 (2004).
[4] O. Bunk *et al.*, Phys. Rev. B **59**, 12 228 (1999).
[5] J.-H. Cho *et al.*, Phys. Rev. B **64**, 235302 (2001).
[6] J. Nakamura, S. Watanabe, and M. Aono, Phys. Rev. B **63**, 193307 (2001).
[7] R. H. Miwa and G. P. Srivastava, Surf. Sci. **473**, 123 (2001).
[8] S. Wang *et al.*, Phys. Rev. B **68**, 035329 (2003).
[9] K. Fleischer *et al.*, Phys. Rev. B **67**, 235318 (2003).
[10] J.-H. Cho, J.-Y. Lee, and L. Kleinman, Phys. Rev. B **71**, 081310(R) (2005).
[11] S.-F. Tsay, Phys. Rev. B **71**, 035207 (2005).
[12] X. Lopez-Lozano *et al.*, Phys. Rev. B **73**, 035430 (2006).
[13] S. J. Park *et al.*, Phys. Rev. Lett. **95**, 126102 (2005).
[14] J. Guo, G. Lee, and E. W. Plummer, Phys. Rev. Lett. **95**, 046102 (2005).
[15] C. Gonzalez, F. Flores, and J. Ortega, Phys. Rev. Lett. **96**, 136101 (2006).
[16] A. A. Stekolnikov *et al.*, Phys. Rev. Lett. **98**, 026105 (2007).
[17] G. Lee *et al.*, Phys. Rev. B **70**, 121304(R) (2004).
[18] S. S. Lee *et al.*, Phys. Rev. Lett. **88**, 196401 (2002).
[19] S. V. Ryjkov *et al.*, Surf. Sci. **488**, 15 (2001).
[20] T. Kanagawa *et al.*, Phys. Rev. Lett. **91**, 036805 (2003).
[21] T. Uchihashi and U. Ramsperger, Appl. Phys. Lett. **80**, 4169 (2002).
[22] T. Tanikawa *et al.*, Phys. Rev. Lett. **93**, 016801 (2004).
[23] http://www.pwscf.org/
[24] A. Calzolari *et al.*, Phys. Rev. B **69**, 035108 (2004).
[25] Y.-S. Lee, M. Buongiorno Nardelli, and N. Marzari, Phys. Rev. Lett. **95**, 076804 (2005).
[26] S. Riikonen, A. Ayuela, and D. Sanchez-Portal, Surf. Sci. **600**, 3821 (2006).
[27] S. Wippermann *et al.*, Surf. Sci. **601**, 4045 (2007).

[28] We calculated the influence of the adatom-localized surface phonons—obtained from frozen-phonon calculations—on the electron transmittance for RT occupation. The impact is different, ranging from a reduction by about one tenth for some of the In adatom modes to nearly no influence at all for the hydrogen vibrations.