

Influence of Na adsorption on the quantum conductance and metal-insulator transition of the In-Si(111)(4 × 1)–(8 × 2) nanowire array

W. G. Schmidt, M. Babilon, C. Thierfelder, S. Sanna, and S. Wippermann

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

(Received 26 May 2011; published 14 September 2011)

Density functional theory calculations are performed to study the influence of Na adatoms on the electron transport and structural properties of the In-Si(111)(4 × 1)–(8 × 2) nanowire array. It is found that there are several energetically nearly degenerate Na adsorption sites, the precise energetic ordering of which depends on the surface coverage. Irrespective of the adsorption site, the adatoms show mainly a repulsive interaction with little indications for long-range correlation. The calculations show only a moderate disturbance of the quantum conductance of the metallic room-temperature (4 × 1) In nanowire phase upon Na adsorption. Also, the electronic density of states at the Fermi energy is only slightly modified. However, it is found that adsorption-induced strain as well as charge donation into the In nanowires lead to a noticeable decrease of the metal-insulator transition temperature. Therefore, Na adsorption on the semiconducting (8 × 2) In nanowire phase may trigger a transition into the metallic state.

DOI: [10.1103/PhysRevB.84.115416](https://doi.org/10.1103/PhysRevB.84.115416)

PACS number(s): 68.43.Bc, 73.20.At, 73.63.–b

The increasing perfection in the atomic-scale fabrication and modification of low-dimensional nanostructures has brought about a strong interest in understanding and predicting the electronic properties of quasi-one-dimensional systems. The ordered array of In nanowires that self-assembles at the Si(111) surface—first described in 1965¹—is one of the most fascinating and intensively studied model systems in this context. On the one hand, it provides a robust test bed for studying electron transport at the atomic scale.^{2–6} On the other hand, the reversible phase transition from the metallic Si(111)-(4 × 1)-In zigzag chain structure [see Fig. 1(a)] formed at room temperature (RT) to an insulating (8 × 2) reconstruction below 120 K⁷ has provoked many fundamental questions and intensive research. The structural details of the low-temperature (LT) (8 × 2) phase as well as the mechanism and cause of the metal-insulator transition (MIT) have remained elusive for a long time. Finally, density functional theory (DFT) calculations by Gonzalez *et al.*⁸ led to a hexagon model [see Fig. 1(b)] for the insulating phase that accounts well for the available experimental data, as shown, e.g., in Refs. 9 and 10. *First-principles* molecular-dynamics simulations⁸ suggest that the (4 × 1)–(8 × 2) phase transition is due to the “dynamical fluctuations” the system undergoes when, at high temperature, it fluctuates chaotically between degenerate ground states. More recently, the phase transition has been explained as being driven by the subtle balance between the energy lowering due to the hexagon formation and the larger vibrational entropy of the zigzag chains.¹¹ Based on this understanding it has now become possible to tackle the many open questions related to the impact of external perturbations such as adatoms or optical doping³ on the In nanowires.

Ten years ago, it was noted that tiny amounts of adsorbates, specifically less than 0.1 monolayers (ML) of Al, Ga, In, or Ag adatoms, revert the LT (8 × 2) phase to the (4 × 1) structure usually observed above 120 K.¹² The structural modification was found to be accompanied by an increase in electrical conductivity. More recent studies^{13,14} report a decrease of the MIT transition temperature T_C upon In adsorption, while

the exposure of the In nanowires to oxygen was found to increase T_C . Intriguing indirect interactions between the adatoms mediated by the In nanowire charge-density wave (CDW) were observed for Pb (Ref. 15) and Co (Ref. 2) adsorption. It is likely that most studies in the context of atomic adsorption on the In nanowire array are devoted to the influence of sodium. Using scanning tunneling microscopy (STM), Lee *et al.*¹⁶ found that the metallic (4 × 1) In zigzag chain structure turns in an insulating system with a doubled periodicity along the chains upon Na deposition. This was attributed to an adsorbate-induced CDW pinning. Density functional calculations by Cho, Oh, and Kleinman,¹⁷ however, found the doubling of the periodicity energetically unfavorable and did not support a Na-induced metal-insulator transition resulting from a CDW gap. In 2008, temperature-dependent low-energy electron diffraction (LEED) data were interpreted in terms of an increase of the transition temperature T_C due to Na adsorption,¹⁸ confirming the trend reported in Ref. 16. In fact, a value of $T_C = 186$ K was reported for the adsorption of 0.1 ML Na. In clear contrast, Shim *et al.*⁴ as well as a very recent study by Yeom and co-workers¹⁹ found an almost linear decrease of T_C with the amount of Na atoms deposited on the In nanowire array. In Ref. 4, a variation between 125 and 90 K is reported for T_C . In Ref. 19, a (4 × 1) LEED pattern was detected at heavily alkali-metal-doped In-Si(111) even at 50 K. While DFT calculations have contributed greatly to the understanding of the clean nanowire array, see, e.g., Refs. 8–11,20–24, we are aware of only relatively few studies addressing computationally the adsorption of adatoms on the nanowires.^{6,15,17,25}

In order to contribute to a better understanding of the effect of adsorbates on the properties of In nanowire, we perform *first-principles* calculations on the structural and electronic properties as well as quantum conductance of the Na decorated In-Si(111)(4 × 1)–(8 × 2) nanowire array. In detail, we perform DFT calculations within the local density approximation²⁶ as implemented in the Vienna Ab-initio Simulation Package (VASP).²⁷ We follow Stekolnikov *et al.*⁹ concerning the numerical details of the total-energy

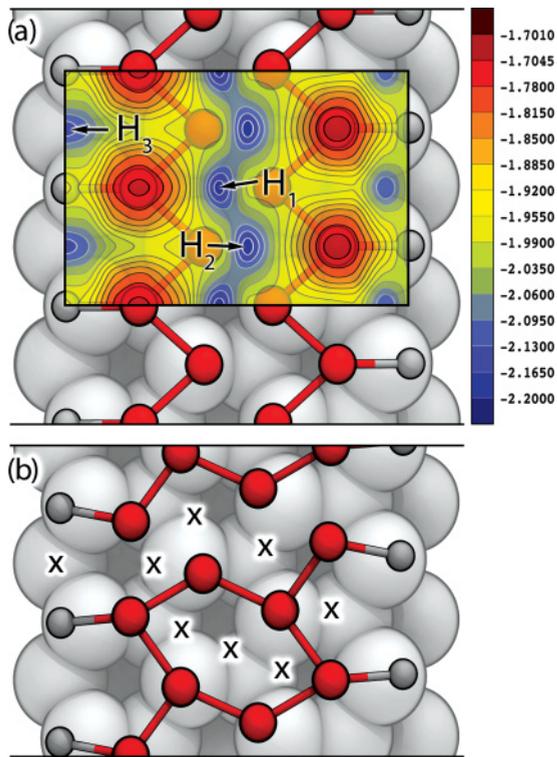


FIG. 1. (Color online) (a) Potential energy surface (in eV) calculated for Na adatoms on the In/Si(111)(4 × 1) surface. The two local minimum energy positions for the adsorbed species are marked. Dark and light balls indicate In and Si positions, respectively. (b) Starting configurations for Na adatoms on the In/Si(111)(8 × 2) surface.

calculations. The Landauer conductance in the limit of zero bias is computed using the WanT approach,²⁸ i.e., a Green function formalism based on *maximally localized Wannier functions*^{29,30} as a minimal basis set. Thereby, we exploit the fact that the In-related surface states close to the Fermi energy depend very little on the substrate³¹ and study model structures that contain only the In nanowires attached to a single Si bilayer, with the remaining Si dangling bonds terminated with hydrogen. Test calculations for structures with two Si bilayers³² confirm the validity of this approach.

We start by determining the potential energy surface (PES) for Na adsorbed on the RT (4 × 1) phase of the nanowire array. These calculations are performed in a (4 × 4) unit cell with three bilayers of Si. The calculated energy landscape and the most favored lateral positions for the adspecies are shown in Fig. 1(a). For one Na adatom per (4 × 4) unit cell, we find three nearly degenerate adsorption sites H_1 , H_2 , and H_3 with adsorption energies of 2.165, 2.150, and 2.174 eV, respectively. At this as well as higher coverages, sodium prefers a position between neighboring In and Si chains (H_3). Lowering the coverage to one Na adatom per (8 × 4) unit cell leads to H_1 being the most stable adsorption site. Our results agree qualitatively with earlier DFT calculations of the Kleinman group,¹⁷ which—using a (4 × 3) unit cell and the generalized gradient approximation—reported adsorption energies of 1.452 and 1.446 eV for adsorption at the H_1 and H_2 site, respectively, while the adsorption between the In and

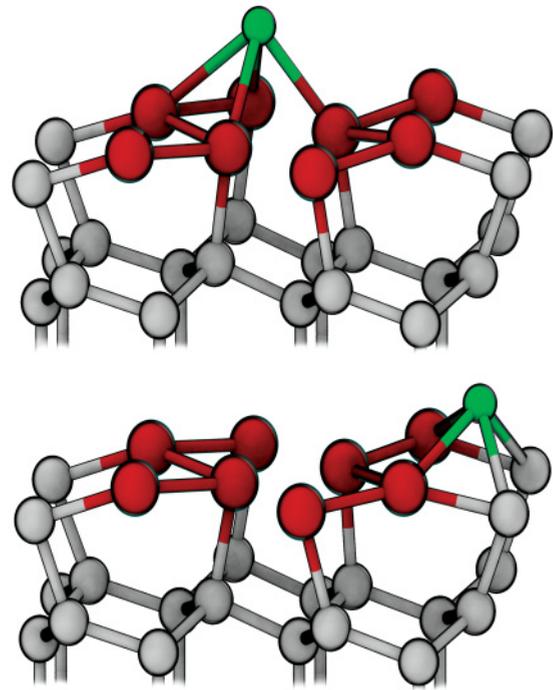


FIG. 2. (Color online) Equilibrium structure of Na adsorbed on the In-Si(111)(4 × 1) surface at the H_1 (top) and H_3 (bottom) site.

Si zigzag chains was found to be less favored. The corrugation of the PES with a distinct channel along the chain direction suggests a strongly anisotropic diffusion behavior and a high adatom mobility along the In zigzag chains.

The two energetically most relevant structures, H_1 and H_3 , are schematically shown in Fig. 2. Obviously, Na prefers a pyramidal configuration. The structural deformations of the In nanowire array are comparatively minor. The largest deviation from the ground-state geometry of the clean In-Si(111)(4 × 1) surface occurs in the case of the H_1 adsorption and modifies the In-In distance across the two parallel zigzag chains by about 0.16 Å.

In order to probe long-range correlation effects between surface adsorbed adatoms possibly due to adsorbate-induced Friedel oscillations,³³ we performed calculations for different adatom distances along and perpendicular to the In chains. The results are summarized in Fig. 3. Sodium adsorbed in the $H_{1/3}$ position was calculated using a (4 × n) translational symmetry with $n = 1, 2, 3, 4, 5, 6$. In the case of H_1 adsorption, it is found that the adsorption energy increases monotonously with increasing distance, at least for the distances that are computationally accessible. In the case of H_3 , two rather shallow energy minima are found for $n = 3, 5$. If the adatom distance is increased vertically to the In chains, the energetic order of the two adsorption sites may change: H_1 adsorption is more favored than H_3 adsorption for an (8 × 4) surface periodicity. While the details of the adsorption geometry will thus depend on the surface coverage as well as the adsorption kinetics, there is a clear overall trend for increased adsorption energy with increased adatom separation. Similar results were obtained in Ref. 17 and explained by an electron transfer from the Na adatoms in the In-chain derived orbitals. Thus, adsorbed Na atoms become effectively positive ions, giving

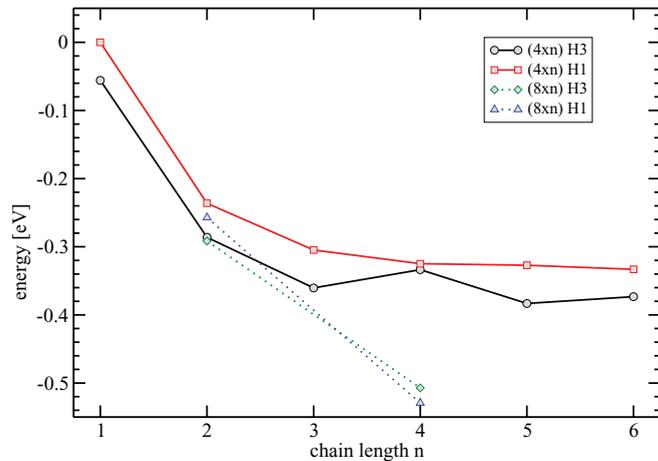


FIG. 3. (Color online) Change of the adsorption energy upon increasing the distance between adatoms adsorbed in the H_1 position for $(4/8 \times n)$ translational symmetry.

rise to a repulsion interaction. The stability of semiconductor surface reconstructions is often surprisingly well described by the Madelung energy of surface atoms charged according to the electron counting rule; see, e.g., Refs. 34 and 35. Assuming a similarly simple picture holds here, we calculated the Coulomb repulsion for a periodic lattice of positively charged Na adatoms, assuming a screening that is approximately given by half the static dielectric constant of Si (due to the reduced screening at the surface). Using the charge transfer as a fit parameter, it is found that the data of Fig. 3 are well described for a charge transfer of about $0.8e$. Certainly, the result of such a procedure has to be taken with caution. Nevertheless, it fits well with the interpretation of angle-resolved photoemission spectroscopy (ARPES) data given in Ref. 19. Here, it was concluded that roughly a single electron is donated to the surface from each Na adsorbate atom.

The impact of Na adatoms on the In nanowire electronic properties is a controversial subject. There are reports that Na deposition increases¹⁸ as well as decreases^{4,19} the MIT transition temperature T_C . Morikawa *et al.*¹⁹ performed STM studies and discriminated between two effects of the Na deposition, namely the global suppression of the metal-insulator transition versus a local lattice distortion that results in a reduced density of states (DOS) at the Fermi energy. While in Ref. 19 it is stated that in spite of the reduced DOS at the Fermi energy, the In nanowire remains metallic, the opening of a small gap of about 0.1 eV has been concluded from high-resolution electron-energy-loss spectra.¹⁶

Before we address the impact of the adsorbate atoms on the phase-transition temperature, we discuss its local influence on the nanowire electronic properties. Thereby, we start from the relaxed adatom positions H_1 as well as H_3 and consider single Na adatoms calculated in a (4×8) surface unit cell. The lower part of Fig. 4 shows the electronic density of states (DOS) of the Na decorated In-Si(111) (4×1) surface in comparison with the DOS of the clean In-Si(111) (4×1) surface. Obviously, the modification of the DOS is negligible in the intermediate vicinity of the Fermi energy. The metallicity of the nanowires is not affected by the alkali-metal adsorption. However, about 0.1 eV below the Fermi energy, a clear

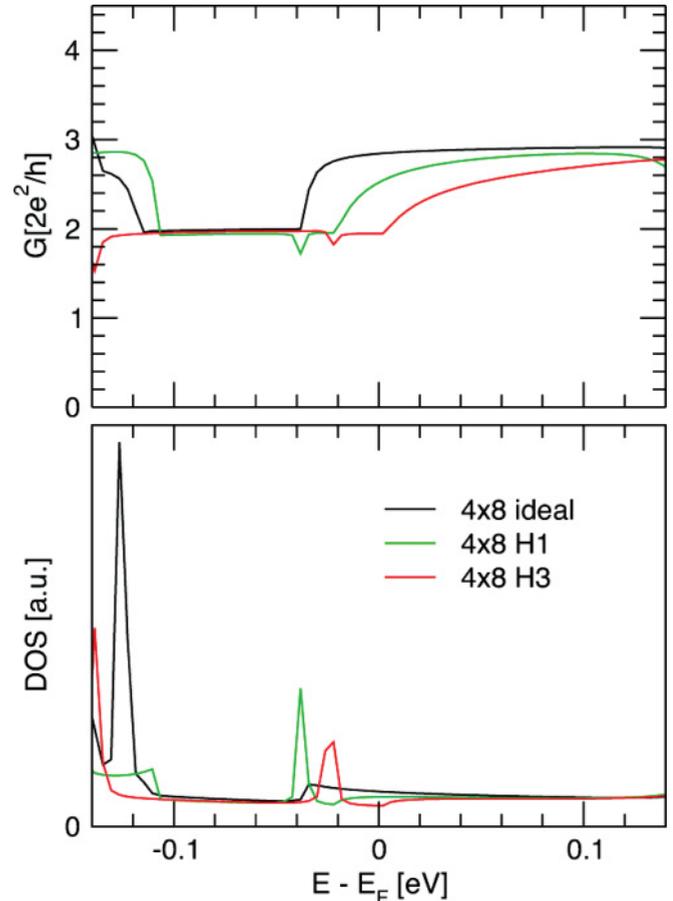


FIG. 4. (Color online) Quantum conductance spectrum for electron transport along the wire direction (upper part) and total density of states (lower part) calculated for ideal and adatom-modified In/Si(111) structures.

reduction in the DOS is calculated for the Na adsystem, both for H_1 and H_3 adsorption. This confirms earlier DFT calculations by the Kleinman group¹⁷ performed for smaller unit cells, i.e., higher Na coverages. The change of the DOS calculated here may explain high-resolution electron-energy-loss spectroscopy (HREELS) findings for Na-adsorbed nanowires demonstrating that the Drude tail due to transitions near the Fermi level is drastically reduced in width compared to the clean surface (from 33.6 to 11.5 meV).¹⁶

A modification of the surface conductivity does not necessarily require a change in the density of states near the Fermi level, but may also arise, e.g., from potential well scattering or structure deformation effects.⁶ In order to see whether such effects are to be expected in the present case, the influence of the Na adatoms 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 (4×8) wire segment] and the semi-infinite leads are modeled with ideal In nanowires. The calculated conductance spectra of the ideal and Na adatom perturbed In nanowires (H_1 and H_3 geometries) are shown in the upper part of Fig. 4. 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.^{5,36,37} 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, and are therefore not expected to substantially mask trends derived from calculations for clean and adatom-decorated In nanowires. Compared to the calculations for the ideal structure, a reduction of the quantum conductance at E_F by about one-tenth (H_1) to one-third (H_3) compared to the ideal chain is obtained here for the case of Na adatoms. Comparing these data with similar calculations for Pb, O, In, and H adsorbed on the nanowires,⁶ one finds that sodium is about as effective as Pb in hindering the electron transport through the wires. Hydrogen adsorption affects the electron transport less while In and O are more effective scatterers.

Finally, we discuss the influence of the Na adatoms on the phase transition. We adsorbed sodium on the structure of the LT (8×2) phase of In-Si(111). Thereby, we used the lateral positions indicated in Fig. 1(b) as starting configurations. Structural relaxation leads to a variety of local energy minima. Interestingly, the transformation of the In hexagon structure in the zigzag-chain geometry of the (4×1) phase with the Na adatom assuming the H_1 position shown in Fig. 1(a) represents the global energy minimum among the necessarily limited number of structures investigated. Thus, the alkali-metal adsorption seems to perturb the subtle energy balance between the semiconducting In hexagons and the metallic In zigzag chains in favor of the latter.

The changes in the calculated electronic band structure accompanying the (4×1)–(8×2) phase transition are shown in Fig. 5. In agreement with earlier studies, e.g., Ref. 23, we find the hexagon formation to be related to the opening of a small gap. The charge transfer from the adatoms into the surface lowers the gain in band-structure energy upon hexagon formation. This could be one plausible mechanism that explains why Na adsorption tends to favor the formation of the (4×1) phase. In order to verify this assumption, we

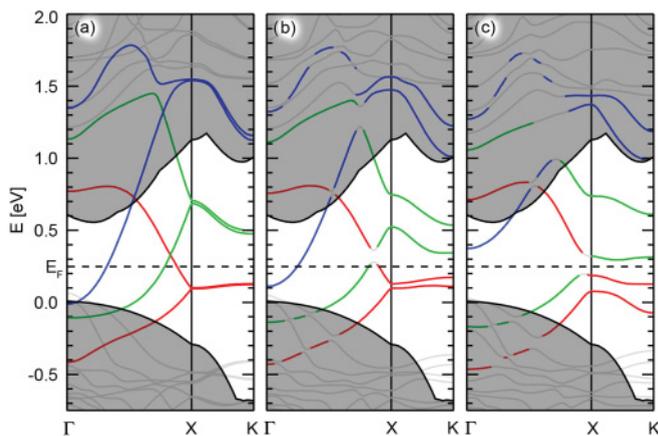


FIG. 5. (Color online) Band structures of the zigzag chain (a) and hexagon model (c) of the In-Si(111) surface calculated within a (4×2) surface unit cell. The electron bands of a transitional structure obtained from the superposition of the phonon modes that transform between these structural models (see Ref. 11) are shown in (b). Bands of equal color are characterized by similar wave functions.

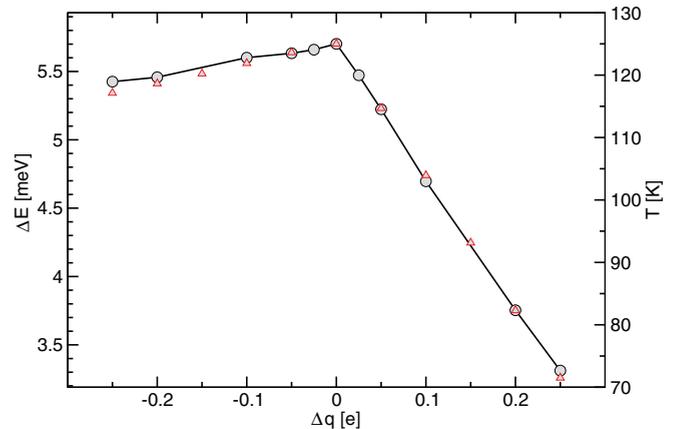


FIG. 6. (Color online) Difference in total energy (per surface atom) between In-Si(111)(4×1) and In-Si(111)(8×2) surfaces depending on the surface charging [electrons per (8×2) surface unit cell]. The right scale indicates the phase-transition temperature predicted for the respective charging on the assumption that the adatoms modify the vibrational entropy of (4×1) and (8×2) surfaces by the same amount. Circles and triangles indicate energies obtained with and without structural relaxation, respectively.

follow Ref. 38 and calculate the energy difference between (4×1) and (8×2) reconstructed In-Si(111) surfaces—in the absence of any alkali-metal adatoms—depending on the surface charging. The results are shown in Fig. 6. Obviously, the charging of the surface destabilizes indeed the (8×2) surface with respect to the (4×1) phase. However, even a strong charge transfer of $0.2e$ is not sufficient to quench the total-energy difference between In-Si(111)(4×1) and In-Si(111)(8×2) surfaces. The spontaneous lifting of the hexagon geometry observed during the structural relaxation of the Na decorated In nanowire array is therefore probably not caused entirely by the charge transfer, but will also be related to local strain.

The ground state of the surface-supported nanowires is characterized by the minimum of the free energy F as a function of the substrate crystal volume V and the temperature T . Within the adiabatic approximation, F is given by

$$F(V, T) = F_{\text{el}}(V, T) + F_{\text{vib}}(V, T), \quad (1)$$

with $F_{\text{el}} = E_{\text{tot}} - TS_{\text{el}}$, where the total energy E_{tot} can be approximated by the zero-temperature DFT value. The electronic entropy S_{el} was shown earlier to play only a minor role in the energy balance of the In nanowire array. In fact, it shifts the phase-transition temperature T_C by less than 5 K.¹¹ If one assumes that the adsorption of Na atoms changes the vibrational energy of In-Si(111)(4×1) and In-Si(111)(8×2) surfaces by a similar amount due to the appearance of new localized phonon modes and neglects any influence of local strain on the phase stability, the change of the phase-transition temperature can be estimated from the modification of the difference of the respective total energies upon charge transfer into the surface calculated above. We thus obtain the phase-transition temperatures indicated on the right-hand side in Fig. 6. From the data shown in Fig. 6, we would thus predict a phase-transition temperature of $T_C = 97$ K for a Na coverage

of 0.01 ML. Given that—as argued above—the local strain induced by the Na adsorption also favors In zigzag chains rather than hexagons, this temperature should be considered an upper limit for the actual value. Unfortunately, the present experimental findings do not allow for a direct comparison, as no detailed information on the coverage-dependent value of T_C is available. The order of magnitude predicted here, however, seems to agree with the recent experimental data reported in Refs. 4 and 19.

On the other hand, Na deposition at very low temperatures will not necessarily lead to the ground-state geometry where local strains favors the zigzag chain formation. It is very well conceivable that Na adsorption at some metastable position leads to geometrical constraints that favor hexagons and thus leads to an apparent pinning of the In-Si(111)(8×2) surface. On the other hand, the above estimation of the variation of T_C due to Na adsorption rests on the model for the phase transition proposed by Wippermann and Schmidt,¹¹ i.e., the competition between band-structure energy and vibrational free energy. If one follows the dynamical fluctuation model⁸ for the phase transition, the influence of adsorbed sodium on the vibrational properties of the In nanowires will be much more important for T_C . Since additional atoms can be expected to hinder the dynamical fluctuations between the ground-state geometries, an increase rather than a decrease of T_C might be observed. In this context, careful measurements of the actual influence of Na on the phase-transition temperature may help to determine the correct model for the phase transition.

If one sticks to the Wippermann model for the phase transition, it is clear from Fig. 6 that a reduction of the phase-transition temperature should also occur in the case of p doping. This appears plausible in the picture discussed above, because the energetic preference of the insulating (8×2) reconstructed In-Si(111) surface over the metallic (4×1) will be reduced no matter which direction the Fermi energy is shifted. However, we are not aware of an experimental study in this context.

To summarize, density functional theory calculations on the Na decorated In-Si(111)(4×1)-(8×2) nanowire array find a strong influence of alkali-metal adsorption on nanowire properties. This concerns in particular the low-temperature (8×2) phase, which gets destabilized due to the charge transfer from the adatoms into the In nanowires as well as due to local strain. This leads to a decrease of the phase-transition temperature and may trigger an insulator-metal transition at specific temperatures. Adsorption of Na on the room-temperature (4×1) phase, on the other hand, leads to a slight reduction of the surface conductivity as well as to a distinct decrease of the density of electronic states below the Fermi energy. The surface remains clearly metallic, however. The calculations indicate a strong Coulomb repulsion between the Na adatoms.

We gratefully acknowledge financial support from the DFG as well as supercomputer time provided by the HLRS Stuttgart and the Paderborn PC².

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