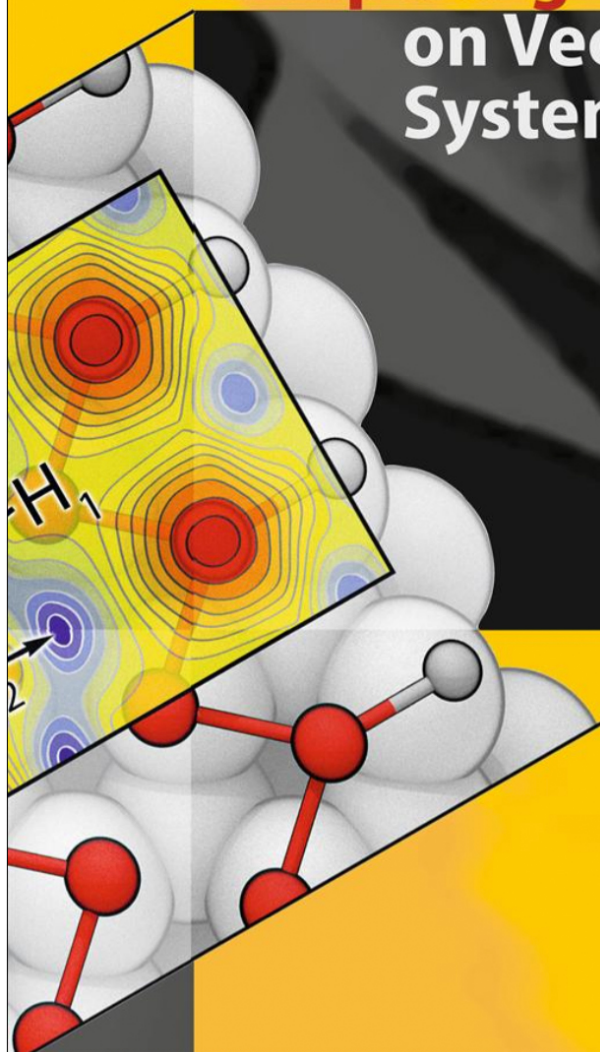


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Influence of Adatoms on the Quantum Conductance and Metal-Insulator Transition of Atomic-Scale Nanowires

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

Abstract Using the adsorption of Na adatoms on the Si(111)(4×1)-(8×2) nanowire array as an example, density functional theory calculations are performed to study and understand the influence of adatoms on the quantum conductance and metal-insulator transition of atomic-scale nanowires. It is found that there are several energetically nearly degenerate Na adsorption sites, the precise energetical 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 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.

1 Introduction

The increasing perfection in the atomic-scale fabrication and modification of low-dimensional nanostructures drives a strong interest in understanding and predicting the electronic properties of quasi-1D systems. The ordered array of In nanowires that self-assembles at the Si(111) surface – first described in 1965 [1] – is one of the most fascinating and most intensively studied model systems in this context. On the one hand, it provides a robust testbed 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. 1a) formed at room temperature (RT) to an

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insulating (8×2) reconstruction below 120 K [7] 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) remained elusive for a long time. Finally, density functional theory (DFT) calculations by Gonzalez et al. [8] led to a hexagon model (see Fig. 1b) for the insulating phase that accounts well for the available experimental data as shown, e.g., in [9, 10]. Recently, the phase transition has been explained as 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 doping [3] on the In nanowires.

Already 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. This is in contrast to more recent studies [13, 14] which report a decrease of the MIT transition temperature T_C upon In adsorption. Also 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 [15] and Co [2] adsorption. Probably 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 [16]. In clear contrast, Shim et al. [4] as well as a very recent study by Yeom and co-workers [19] found an almost linear decrease of T_C with the amount of Na atoms deposited on the In nanowire array. While DFT calculations have contributed greatly to the understanding of the clean nanowire array, see, e.g., [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].

2 Computational Method

In order to contribute to a better understanding of the effect of adsorbates on the In nanowire properties 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 approximation [26] 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 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 substrate [31] 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 bilayers [32] confirm the validity of this approach.

3 Results

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. 1a. 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 1.165, 1.150 and 1.174 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 largely agree with earlier DFT calculations of the Kleinman group [17] which – using a (4×3) unit cell – 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 Si zigzag chains was found to be somewhat less favoured than in the present work. 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 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 $H_{1/3}$ position was calculated using a ($4 \times n$) translational symmetry with $n = 1, 2, 3, 4, 5, 6$. In case of H_1 adsorption it is found that the adsorption energy is monotonously increasing with increasing distance, at least for the distances 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 energetical order of the two

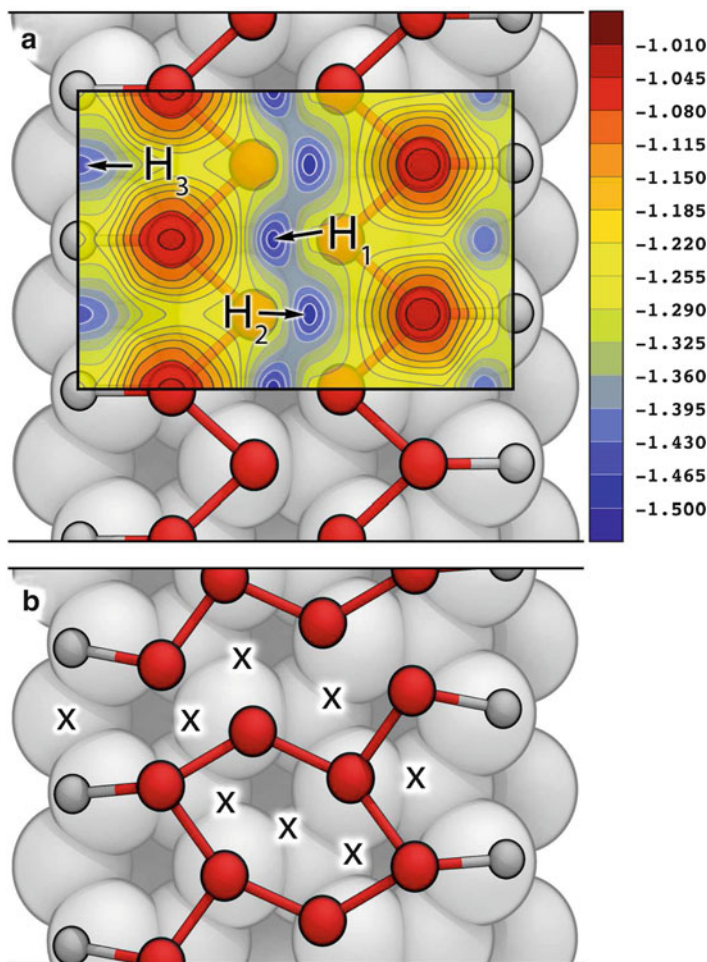


Fig. 1 (a) Potential energy surface (in eV) calculated for Na adatoms on the In/Si(111)(4×1) surface. The two local minimum energy positions for the adsorbed species are marked. Dark and light balls indicate In and Si positions, respectively. (b) Starting configurations for Na adatoms on the In/Si(111)(8×2)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

adsorption sites may change: H_1 adsorption is more favored than H_3 adsorption for a (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 [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 rise to a repulsion interaction. The stability of semiconductor surface reconstructions is often surprisingly well described by the

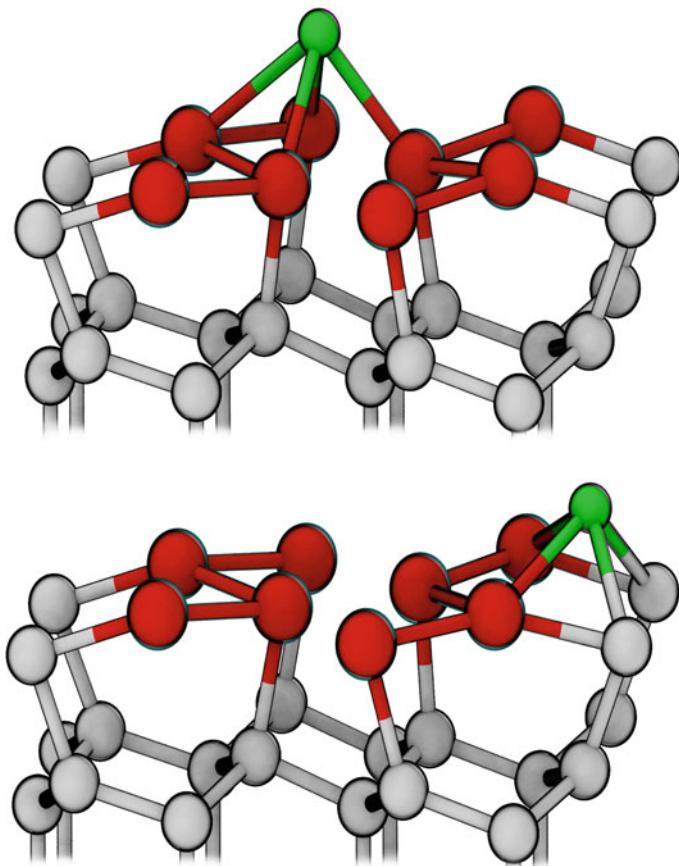


Fig. 2 Equilibrium structure of Na adsorbed on the In-Si(111)(4×1) surface at the H_1 (top) and H_3 (bottom) site (color online)

Madelung energy of surface atoms charged according to the electron counting rule, see, e.g. [34,35]. Assuming a similarly simple picture to hold 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 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 to the interpretation of angle-resolved photoemission spectroscopy (ARPES) data given in [19]. Here it was concluded that roughly a single electron is donated to the surface from each Na adsorbate atom.

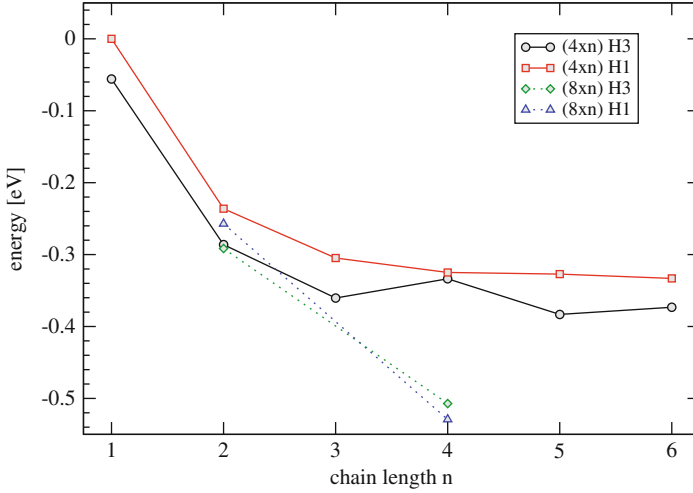


Fig. 3 Change of the adsorption energy upon increasing the distance between adatoms adsorbed in H_1 position for $(4 \times n)$ translational symmetry. Calculated values are shown as circles, the lines represent simply a guide to the eye (color online)

The impact of Na adatoms on the In nanowire electronic properties is controversially discussed. There are reports that Na deposition increases [18] 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, the global suppression of the metal-insulator transition vs. a local lattice distortion that results in a reduced density of states (DOS) at the Fermi energy. While in [19] it is stated that in spite of the reduced DOS at the Fermi energy the In nanowire remain 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 adsorption. However, about 0.1 eV below the Fermi energy a clear 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 group [17] performed for smaller unit cells, i.e., higher Na coverages. The change of the DOS calculated here also agrees with 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].

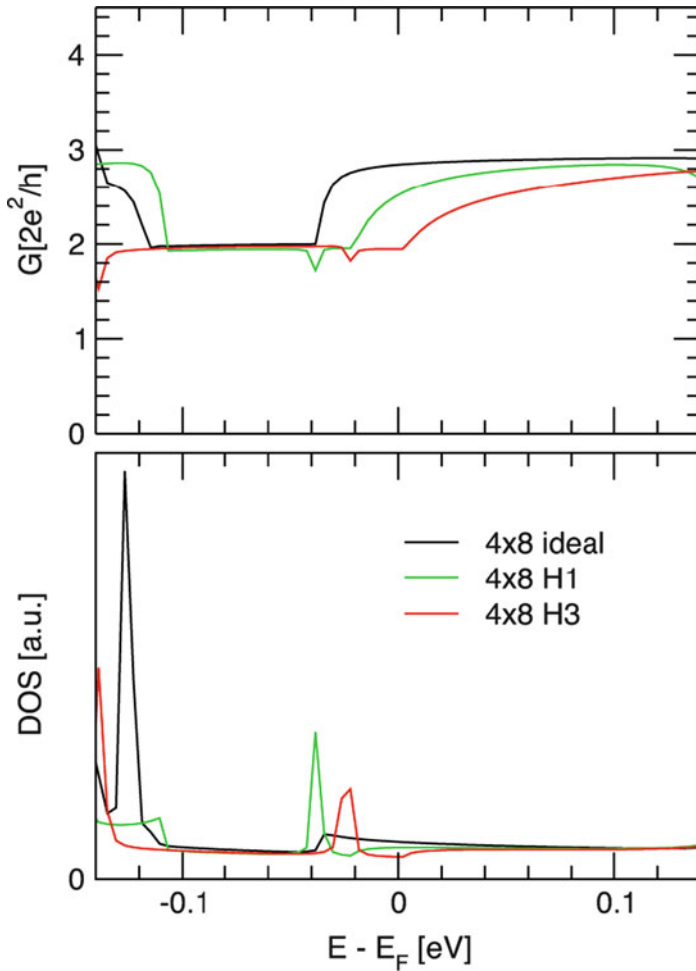


Fig. 4 Quantum conductance spectrum for electron transport along the wire direction (*upper part*) and total density of states (*lower part*) calculated for ideal and adatom-modified In/Si(111) structures (color online)

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

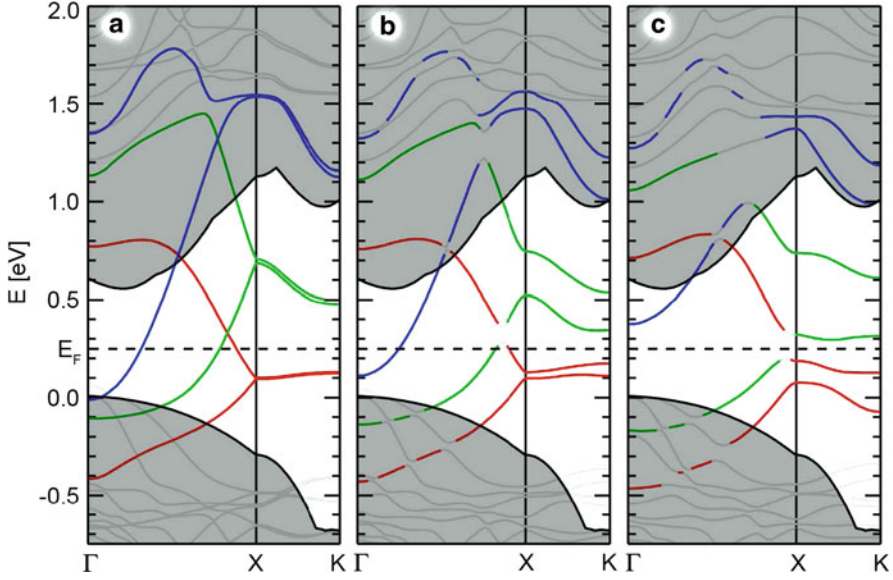


Fig. 5 Band structures of the zigzag chain (a) and hexagon model (c) of the In-Si(111) surface calculated within a (4×2) surface unit cell. The electron bands of a transitional structure obtained from the superposition of the phonon modes that transform between these structural models (see [11]) is shown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

Fig. 4. The transmittance at E_F calculated for the unperturbed nanowire somewhat overestimates – by roughly a factor of two – 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 so 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 fifth (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. 1b as starting configurations. Structural relaxation leads to 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. 1a represents the global

energy minimum among the necessarily limited number of structures investigated. Thus, the alkali 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 $(4 \times 1) - (8 \times 2)$ phase transition are shown in Fig. 5. In agreement with earlier studies, e.g. [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 follow [38] and calculate the energy difference between (4×1) and (8×2) reconstructed In-Si(111) surfaces – in the absence of any alkali adatoms – in dependence 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 can therefore not entirely be caused 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 adiabatic approximation F is given by

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

with $F_{el} = E_{tot} - TS_{el}$, where the total energy E_{tot} can be approximated by the zero-temperature DFT value. The electronic entropy S_{el} was earlier shown 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. Given that – as argued above – the local strain induced by the Na adsorption also favors In zigzag chains rather hexagons, the temperatures indicated in Fig. 6 could be considered an upper limit for the actual values.

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. In any event, a strong reduction of T_C scaling nearly linearly with Na deposition is clearly found in [4]. Here a variation between 125 and 90 K is reported for T_C . Another study reports an even more drastic modification of T_C . In [19] a 4×1 LEED pattern was detected at heavily alkali-doped In-Si(111) even at 50 K. Thus, the calculated T_C values of Fig. 6 seem to be at least of the correct order of magnitude. On the other hand, Na deposition at very low temperatures will not

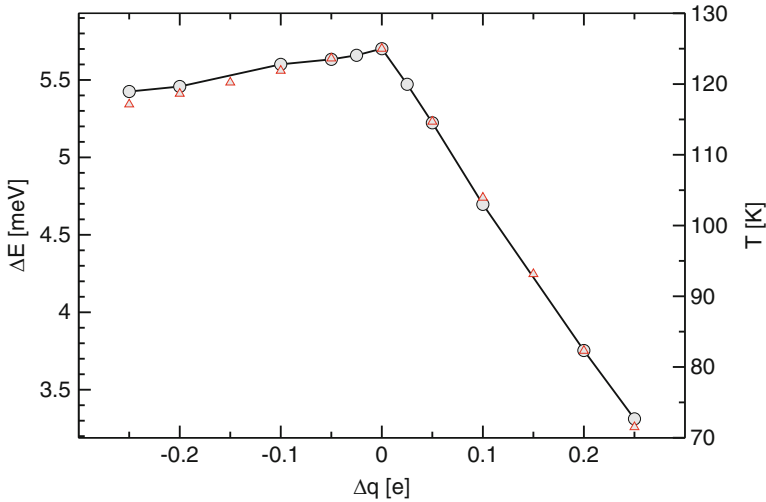


Fig. 6 Difference in total energy (per surface atom) between In-Si(111)(4 × 1) and In-Si(111)(8 × 2) surfaces in dependence on the surface charging. The right scale indicates the phase transition temperature predicted for the respective charging on the assuming that the adatoms modify the vibrational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

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 lead to an apparent pinning of the In-Si(111)(8 × 2) surface.

From Fig. 6 it is clear that a reduction of the phase transition temperature should also occur in 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 in 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 the alkali adsorption on the 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.

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References

1. J J Lander and J Morrison, *J. Appl. Phys.* **36**, 1706 (1965).
2. C Liu, T Uchihashi, and T Nakayama, *Phys. Rev. Lett.* **101**, 146104 (2008).
3. Y Terada, S Yoshida, A Okubo, K Kanazawa, M Xu, O Takeuchi, and Hidemi Shigeoka, *Nano Letters* **8**, 3577 (2008).
4. H Shim, S-Y Yu, W Lee, J-Y Koo, and G Lee, *Appl. Phys. Lett.* **94**, 231901 (2009).
5. T Tanikawa, I Matsuda, T Kanagawa, and S Hasegawa, *Phys. Rev. Lett.* **93**, 016801 (2004).
6. S Wippermann, N Koch, and W G Schmidt, *Phys. Rev. Lett.* **100**, 106802 (2008).
7. 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).
8. C Gonzalez, F Flores, and J Ortega, *Phys. Rev. Lett.* **96**, 136101 (2006).
9. A A Stekolnikov, K Seino, F Bechstedt, S Wippermann, W G Schmidt, A Calzolari, and M Buongiorno Nardelli, *Phys. Rev. Lett.* **98**, 026105 (2007).
10. 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).
11. S Wippermann and W G Schmidt, *Phys. Rev. Lett.* **105**, 126102 (2010).
12. S V Ryjkov, T Nagao, V G Lifshits, and S Hasegawa, *Surf. Sci.* **488**, 15 (2001).
13. W Lee, H Shim, and G Lee, *J. Korean Phys. Soc.* **56**, 943 (2010).
14. T Shibusaki, N Nagamura, T Hirahara, H Okino, S Yamazaki, W Lee, H Shim, R Hobara, I Matsuda, G Lee, and S Hasegawa, *Phys. Rev. B* **81**, 035314 (2010).
15. M Hupalo, T-L Chan, C Z Wang, K-M Ho, and M C Tringides, *Phys. Rev. B* **76**, 045415 (2007).
16. S S Lee, J R Ahn, N D Kim, J H Min, C G Hwang, J W Chung, H W Yeom, S V Ryjkov, and S Hasegawa, *Phys. Rev. Lett.* **88**, 196401 (2002).
17. J-H Cho, D-H Oh, and L Kleinman, *Phys. Rev. B* **66**, 075423 (2002).
18. S S Lee, S Y Shin, C G Hwang, and J W Chung, *J. Korean Phys. Soc.* **53**, 3667 (2008).
19. Harumo Morikawa, C. C Hwang, and Han Woong Yeom, *Phys. Rev. B* **81**, 075401 (2010).
20. R H Miwa and G P Srivastava, *Surf. Sci.* **473**, 123 (2001).
21. S Wang, W Lu, W G Schmidt, and J Bernholc, *Phys. Rev. B* **68**, 035329 (2003).
22. J-H Cho, J-Y Lee, and L Kleinman, *Phys. Rev. B* **71**, 081310(R) (2005).
23. C Gonzalez, J Ortega, and F Flores, *New J. Phys.* **7**, 100 (2005).
24. X Lopez-Lozano, A Krivosheeva, A A Stekolnikov, L Meza-Montes, C Noguez, J Furthmüller, and F Bechstedt, *Phys. Rev. B* **73**, 035430 (2006).
25. S-Y Yu, D Lee, H Kim, J-Y Koo, and G Lee, *J. Korean Phys. Soc.* **48**, 1338 (2006).
26. D M Ceperley and B J Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
27. G Kresse and J Furthmüller, *Comp. Mat. Sci.* **6**, 15 (1996).
28. A Calzolari, N Marzari, I Souza, and M Buongiorno Nardelli, *Phys. Rev. B* **69**, 035108 (2004).
29. N Marzari and D Vanderbilt, *Phys. Rev. B* **56**, 12847 (1997).
30. Y-S Lee, M Buongiorno Nardelli, and N Marzari, *Phys. Rev. Lett.* **95**, 076804 (2005).
31. S Riikonen, A Ayuela, and D Sanchez-Portal, *Surf. Sci.* **600**, 3821 (2006).
32. S Wippermann, W G Schmidt, A Calzolari, M Buongiorno Nardelli, A A Stekolnikov, K Seino, and F Bechstedt, *Surf. Sci.* **601**, 4045 (2007).
33. S Blankenburg and W G Schmidt, *Phys. Rev. B* **78**, 233411 (2008).
34. W G Schmidt, *Appl. Phys. A* **65**, 581 (1997).

- 35. W G Schmidt, Appl. Phys. A **75**, 89 (2002).
- 36. T Uchihashi and U Ramsperger, Appl. Phys. Lett. **80**, 4169 (2002).
- 37. T Kanagawa, R Hobara, I Matsuda, T Tanikawa, A Natori, and S Hasegawa, Phys. Rev. Lett. **91**, 036805 (2003).
- 38. K Seino, W G Schmidt, and F Bechstedt, Phys. Rev. Lett. **93**, 036101 (2004).