Energetics and stability of dangling-bond silicon wires on H passivated Si(100)

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Abstract
We evaluate the electronic, geometric and energetic properties of quasi 1D wires formed by dangling-bonds on Si(100)-H(2 × 1). The calculations are performed with density functional theory (DFT). Infinite wires are found to be insulating and Peierls distorted, however finite wires develop localized electronic states that can be of great use for atomic scale devices. The ground state solution of finite wires does not correspond to a geometrical distortion but rather to an antiferromagnetic ordering. For the stability of wires, the presence of abundant H atoms in nearby Si atoms can be a problem. We have evaluated the energy barriers for intradimer and intrarow diffusion, finding all of them about 1 eV or larger, even in the case where a H impurity is already sitting on the wire. These results are encouraging for using dangling-bond wires in future devices.

1. Introduction
The study and application of molecular devices entail the creation of atomic structures both for the active part of the device as well as for the interface with other devices and the macroscopic scale [1]. To this aim, the creation of dangling-bond (DB) wires is of particular relevance. Using the scanning tunnelling microscope (STM) several groups have achieved the formation of atomic wires on different semiconductor surfaces [2–4], among which Si(100) has received much attention [3, 4] for its properties and its technological use. Using a completely hydrogen-passivated Si(100) surface, controlled hydrogen desorption can be achieved with an STM tip [3, 4]. In this way, atomic-size wires of Si atoms can be created where their properties are very different from the surrounding passivated Si atoms because they have an open-shell configuration. These dangling-bonds lead to electronic quasi 1D surface structures.

The existence of extended structures of aligned dangling-bonds has also led to an intense theoretical activity [5–13]. The interest in these systems stems from their pristine conditions, which allow a complete theoretical study together with the unique physical properties that can be studied. It is well-known that a chain of dangling-bonds leads to extended electronic states that give rise to a partially-filled 1D band. Its 1D character makes it prone to strong correlations and instabilities. Virtually any perturbation will destroy the metallicity of the state opening an electronic band gap at the Fermi level. If the perturbation is due to the electron-vibration coupling, a Peierls distortion [14] will set in, and will have visible consequences in the arrangement of atoms. However, electron–electron correlations are also present, possibly leading to a Luttinger liquid phase, and to magnetic correlations. This fundamental interest is enhanced by the practical consequences of the formation of these dangling-bond wires. In principle, transport of electrons on an otherwise insulating surface might be possible.

Structural experimental data have been obtained for finite wires [3, 4, 15]. The visualization of deformed structures with the STM [3, 15] seems to indicate the existence of strong electron-vibration couplings and the appearance of a Jahn–Teller effect (the counterpart of the extended-system Peierls effect). If an extra charge is included to account for transport, the injected electron propagates, with the
wire deformation leading to small polaron transport [8, 10]. Moreover, solitons have also been predicted as due to the displacement of the domain wall between adjacent domains of distorted atoms [10]. Recently, solitons have also been revealed in more extended atomic structures on Si(100) [15]. Density functional theory (DFT) calculations seem to indicate that finite systems are not subjected to large electron-vibration effects because antiferromagnetic ordering counterbalances the atomic distortions [9, 11].

In the present paper, we perform DFT calculations to explore the stability of these dangling-bond wires on Si(100) with the aim of establishing their possible use in future atomic scale devices. First, we explore infinite wires, allowing them to find the total energy minima as the unit cell periodicity is changed (to allow for different reconstructions) and including spin polarization. We find that in all these cases gaps develop, destroying the metallicity of the ideal dangling-bond wire, in good agreement with previously reported studies [7, 13].

An extra source of electronic localization is the attachment of atomic impurities at the chemically active dangling-bonds. In particular, the abundant quantities of H atoms on the surface can lead to diffusion and to the passivation of the DB-wire. To assess the stability of the wire, we evaluate the reaction pathway to displace one H atom onto the DB-wire. We repeat the same study for finite wires and study their properties with system size, including the H atom diffusion study. Our calculations show some discrepancy on the behaviour with system size of previous calculations [11], hence we have completed our calculations with a thorough comparison with two different DFT implementations, and with different pseudopotential schemes. Our results indicate that the antiferromagnetic ground state will prevail over the Jahn–Teller distorted one. However, it is difficult to conclude on the actual electronic conductance of these systems [6, 16] without a careful electron transport calculation [16]. A summary and conclusions section finalizes the paper.

2. Theoretical method

*Ab initio* calculations were performed within the density functional theory (DFT) framework as implemented in the VASP code [17]. The Perdew–Burke–Ernzerhof form generalized gradient approximation was used for the exchange and correlation functional [18]. Wavefunctions were expanded using a plane-wave basis set with a cutoff energy of 300 eV. Core electrons were treated within the projector augmented wave (PAW) method [19, 20]. The surfaces were modelled using a slab geometry with eight silicon layers in the unit cell. Eight silicon layers give a good compromise between computational burden and electronic accuracy. Indeed, while the total energy of the different structures is largely converged with eight silicon layers, the band structure, and in particular the bulk gap, is only attained at twelve layers. The bottom surface was passivated using two hydrogen atoms per silicon atom. Different unit cells were used for each calculation, as indicated in next sections. The *k*-point sample was varied accordingly to the unit cell. The geometries were optimized until the forces were smaller than 0.01 eV Å⁻¹. Charge transfer and local magnetic moments were calculated using a Bader charge analysis [21].

We performed several tests to ensure the convergence of the results. In particular, in some selected cases we increased the cutoff energy by 20%, and we increased the number of *k*-points. We found that the geometries are converged below 0.01 Å, and the energy differences are correct within 2 meV/DB, which is well below the energy ranges presented in the following. In addition, in order to check the consistency of the results with respect to the chosen method, some calculations have been repeated with the SIESTA implementation of DFT [22, 23], using Troullier–Martins pseudopotentials [24], a double-ζ polarized basis set to expand the valence wavefunctions [25], and an energy cutoff of 200 Ryd to set the real-space mesh size.

3. Infinite dangling-bond wire

We start the discussion with the analysis of the results for an infinite dangling-bond (DB) wire. As shown in figure 1(a), the completely hydrogenated Si(100) forms a (2 × 1) reconstruction by the creation of dimer rows along the y−[110] direction. A DB-wire can be constructed along two perpendicular directions, as we remove a line of hydrogens along the dimer rows direction (y), or perpendicular to it (x;[110]) (figures 1(b) and (c), respectively). To study the DB-wire along the x-direction, we use the (2 × 4) unit cell shown in figure 1(c). The band structure of the system is shown in figure 2(a). With dots we show the bands with weight from the DB-silicons. We can observe that two bands appear in the bulk energy gap, and they mainly come from the DB-silicons. The gap is reduced with respect to the completely passivated surface, but we still obtain 0.66 eV for the direct band gap, and 0.50 eV for the indirect one. In order to study the wire along the y-direction, we start by using a (4 × 1) unit cell (figure 1(b)). In this case the situation qualitatively changes, and we observe a doubly degenerate metallic band crossing the Fermi energy, coming from the DB-silicons (figure 2(b)). The peculiar shape of the dispersion curve of this metallic band can be explained by analysing the competition between p₂ and s electronic coupling and considering the top surface and the sub surface Si atoms with a negligible through-space direct electronic coupling between the Si top atoms [12, 16].

However, the stabilization of the metallic band is only achieved by the constriction imposed by the (4 × 1) unit cell, in which all the atoms belonging to the DB-wire are equivalent. This ideal case can be destabilized by several mechanisms, such as spin polarization or the formation of a charge density wave along the wire direction, which could give rise to a Peierls-like situation [8, 11]. To check these possibilities we have doubled our unit cell in the y-direction to obtain a (4 × 2) cell in which we have two inequivalent DB-silicon atoms.

First, we have calculated the frequencies of the system to check its stability, finding an imaginary frequency, which reveals that the system is in a saddle point. In the mode corresponding to this frequency one of the atoms in the DB-wire goes upwards, while the other goes downwards. If
Figure 1. Cartoons of the completely hydrogenated Si(100) (2 × 1) surface (a), and DB-wires in y∥[110] (b) and x∥[11̅0] (c) directions are shown. In (d) we show the Peierls-like distortion of the DB-wire in the y-direction when using a (4 × 2) unit cell. Cyan balls represent hydrogen atoms, while silicon atoms are represented by red (surface dimers), blue (Si with dangling-bonds), and yellow (the remainder) balls.

Figure 2. Electronic band structures of several DB-wires: (a) wire in the x-direction; (b) wire in the y-direction using the (4 × 1) unit cell (ideal case); wire in the y-direction using the (4 × 2) unit cell in the NM distorted (c) and AFM (d) situations. The dots indicate the weight on the bands of silicons with DBs.
we relax the new unit cell while considering this possibility, we actually find a more stable geometry in which the two atoms in the new distorted wire are separated by 0.78 Å in the vertical direction (figure 1(d)). This new configuration is more stable than the ideal one by 56 meV/DB. The new bandstructure of the system can be seen in figure 2(c). The metallic band of the ideal DB-wire is now split into two bands, opening a direct (indirect) band gap of 0.40 eV (0.37 eV). The new occupied band comes mainly from the DB-silicon in the upper position, while the unoccupied band states mainly come from the Si atom in the down position. Besides the zig-zag distortion of the atoms in the DB-wire, the Si atoms underneath undergo a slight dimerization (figure 1(d)). We have not found any more complicated configuration which could exist when increasing the unit cell size. Actually, the distorted solution resembles the dimer buckling which appears in the non-hydrogenated Si(100) surface, and therefore we believe it is the most stable configuration that can be found by geometrical relaxation of the system.

3.1. Magnetic ground state

Another possibility to destabilize the ideal DB-wire is to have a spin polarization of the system. We have used the \((4 \times 2)\) unit cell, considering ferromagnetic (FM) and antiferromagnetic (AFM) couplings between the atoms in the DB-wire. The FM case is less stable than the ideal DB-wire by 27 meV/DB, but the AFM one is more stable by 41 meV/DB. Each Si atom in the DB-wire has a magnetic moment of 0.50 \(\mu_B\), and couples antiferromagnetically to its neighbours in the wire. In figure 2(d) we show the band structure of the system. It is similar to the distorted case (figure 2(c)), with a direct (indirect) band gap of 0.55 eV (0.50 eV). In this case the occupied band has contributions from the majority spin of one silicon atom in the DB-wire, and the minority of the adjacent, while in the unoccupied band we find the minority spin of the first atom, and the majority of the second. It is interesting to note that both mechanisms of wire destabilization are not compatible. The relaxed geometry of the AFM wire is essentially identical to the ideal case in a \((4 \times 1)\) unit cell. Inducing a zig-zag distortion within the wire progressively decreases the magnetic moment of the atoms, until it completely disappears with a vertical separation of the atoms of 0.50 Å. A spin polarization solution cannot be stabilized with the relaxed distorted geometry.

The results presented so far have been obtained by using the VASP code. We have also repeated the calculations with the SIESTA implementation of DFT, obtaining the same qualitative results. The quantitative data are presented in table 1. Our results confirm previous experimental and theoretical data. Watanabe et al [5] predicted the Peierls instability in this system. Hitosugi et al [3] experimentally constructed finite DB-wires, and observed a lattice distortion which was described by a Jahn–Teller mechanism. Other theoretical groups have also performed calculations on the system. All the previous results, together with ours, are presented in table 1.

### Table 1. Calculated height difference \(\Delta d_{up-dw} (\text{Å})\) between up and down atoms in the distorted DB-wire, direct and indirect band gap energy \(E_g (\text{eV})\), and energy gain \(\Delta E (\text{meV/DB})\) with respect to the ideal NM DB-wire. Several previous results are included.

|                | \(\Delta d_{up-dw}\) (Å) | \(E_g^{\text{direct}}\) (eV) | \(E_g^{\text{indirect}}\) (eV) | \(\Delta E\) (meV/DB) |
|----------------|--------------------------|------------------------------|-------------------------------|------------------------|
| **NM**         |                          |                              |                               |                        |
| distorted a     | 0.16                     | 0.126                        | 0.025                         | 7                      |
| b              | 0.50                     |                              |                               |                        |
| c              | 0.67                     |                              |                               | 105                    |
| d              | 0.74                     | 0.68                         | 0.36                          | 43                     |
| e              | 0.78                     | 0.39                         | 0.49                          |                        |
| **VASP**       |                          |                              |                               |                        |
|                | 0.78                     | 0.40                         | 0.37                          | 56                     |
| **SIESTA**     |                          |                              |                               |                        |
| S              | 0.81                     | 0.45                         | 0.44                          | 61                     |
| F              | 0.63                     |                              |                               | 57                     |
| **AFM**        |                          |                              |                               |                        |
| a              | 0.00                     | 0.63                         |                               |                        |
| b              | 0.00                     | 0.55                         | 0.50                          | 41                     |
| c              | 0.00                     | 0.63                         | 0.60                          | 56                     |

a Reference [5].
b Reference [3].
c Reference [8].
d Reference [7].
e Reference [11].

In all cases the most stable configuration has a band gap, whose size depends on the details of the calculation. In ours (VASP and SIESTA), the distorted case is more stable than the AFM solution by 15 and 5 meV/DB, respectively, while Lee et al [11] find the opposite, with the AFM configuration being more stable by 8 meV/DB. The small energy difference between the solutions of the order of meV reveals that both are competing and, in practice, other effects such as temperature would determine which case could be experimentally observed. To analyse the nature of this competition, Lee and Cho [13] have studied the DB-wires in C and Ge, and they have compared them to the Si case. They have shown that the on-site electron–electron interactions, modelled by a Hubbard-\(U\) term, are the origin of the AFM coupling, and their strength decreases as we go down in the periodic table from C to Ge. The smaller atoms have the larger \(U\). This effect has also been reported in the magnetization of SiC surfaces when an impurity is adsorbed on a DB, showing different behaviour depending on whether the impurity adsorbs on a C atom or a Si one, due to the larger \(U\) of the C atom [26].

The distorted NM case is due to the electron–lattice coupling, which increases following the same sequence. Thus, while for C the AFM case is clearly the most stable, for Ge the distorted configuration is lower in energy. Si is an intermediate case, where a competition between both situations is observed.

3.2. Mechanisms driving the instabilities

The instabilities found for the 1D DB-wire have a common underlying principle that the electronic energy of the system is greatly reduced if a gap opens in the ideal metallic DB-wire. This gap opening is driven either by a geometrical Peierls-like
distortion [14], or by the spin polarization of the electronic states [27].

In the Peierls instability, the geometrical distortion increases the system’s energy, but the gain in electronic energy overcompensates the ionic energy loss. This can be estimated by separating the global energy gain $\Delta E_{\text{Peierls}}$ into electronic, $\Delta E_{\text{elec}}$, and ionic, $\Delta E_{\text{ion}}$, components. The first component can be expressed by the difference between the electronic energy of the distorted and ideal systems. This energy is given by the sum over all occupied electronic states, hence

$$\Delta E_{\text{elec}} = \int_{\text{occ}}^{} E(\text{DOS}_{\text{Peierls}}(E) - \text{DOS}_{\text{ideal}}(E)) \, dE,$$

where DOS refers to the electronic density of states. This quantity is easily evaluated and gives $\Delta E_{\text{elec}} \approx -0.4 \text{ eV}$.

From table 1 we know that the global energy gain $\Delta E_{\text{Peierls}}$ for two DB is $\approx -0.12 \text{ eV}$. So the energy used to distort two DB in the wire is then $\Delta E_{\text{ion}} \approx 0.28 \text{ eV}$.

Similarly, spin polarization is favourable only in certain situations [27]. Typically, the gain produced by the gap opening has to overcome the tendency to pair spins in electronic states. A Stoner-like criterion [27] for local electronic states shows that spin polarization is energetically possible if the intra-atomic Coulomb repulsion, $U$, is larger than the energy spread of electronic states at the Fermi energy. This energy spread is basically the inverse of the DOS at the Fermi energy, $E_F$. Hence, spin polarization becomes energetically favourable when

$$U \times \text{DOS}(E_F) \gg 1.$$

Hence, the larger $U$ is, the more likely it is to find an AFM ground state for the DB-wire. This has been shown to be the case for C(100) DB wires [13]. Diamond surfaces are actually prone to develop AFM groundstates [28] due to the large value of $U$ and the quasi 1D arrangement of atoms on certain surfaces. Indeed, in [13] the computed values of $U$ are 3.45 eV for C DB wires, while only 1.71 eV for the Si ones. Taking $\text{DOS}(E_F) \approx 1.4 \text{ eV}^{-1}$, from the metallic band of the ideal wire, we obtain $U \times \text{DOS}(E_F) \approx 2.4$. Despite being larger than 1, this value is not very big, showing the minor tendency of the Si DB wires to become spin polarized. This argument is closely related to the fact that the energy of the AFM solution is slightly larger than the Peierls one, table 1.

The AFM solution is driven by superexchange due to the second layer Si atoms, ruling out ferromagnetic solutions for the ground state of the DB-wire. It is easy to visualize the superexchange mechanism in these wires, since the second layer has negligible spin polarization and it is covalently bound to the spin polarized DB orbitals. Hence, spins pair between the DB and the second layer atom, while the second layer atom is shared between two neighbouring DB that forcibly have opposite spins to keep the second layer atom unpolarized. See the scheme in figure 3.

3.3. Stability of the wire versus hydrogen diffusion

A crucial aspect to study before considering DB-wires for any technological application is the chemical stability of the system. One of the mechanisms which could destabilize the DB-wires is the surface diffusion of hydrogen atoms, which by bonding with a silicon DB along the wire would eliminate one DB, modifying the wire electronic transport properties [12]. The new H atom could come from several sources. Let us first consider how the diffusion of hydrogen from the adjacent Si in the dimer would affect the stability of the wire in the y-direction.

To perform this study we have used a $(4 \times 8)$ unit cell, with enough atoms in the DB-wire to consider the H impurity as isolated along the wire’s direction. First, we have calculated the energy difference of having one H moving to the DB-wire from the closest position, as shown in panel (c) of figure 4. The final relaxed energy is 0.18 eV higher in energy than the pristine wire, with all H aligned on one side of the row and the other side forming the DB-wire. Creating one H vacancy by displacing it to the DB-wire is not energetically favourable. We have also calculated the energy barrier of the process using the nudged elastic band (NEB) method [29]. The predicted reaction path is shown in the left part of figure 4. The transition state is shown in figure 4(b), and it corresponds to a large barrier of 1.47 eV. Therefore, in principle the DB-wire would be stable versus this kind of process.

Our theoretical barrier of 1.47 eV is in excellent agreement with the measured values of 1.40 eV [30], and 1.46 eV [31]. However, the experimental situation does not correspond to the same situation considered here. Here, we are interested in the intradimer diffusion when an infinite DB-wire is formed. In the experiment, they either have hydrogen atoms at small coverage [30], or a two-DB wire (formed by the desorption of a H$_2$ molecule after a laser pulse) with intradimer diffusion [31]. This last situation corresponds to the one of finite wires, which we will see in section 4.1.

In the case when a hydrogen atom has already jumped to the DB-wire, we may ask what would be the probability for a second H to jump, as shown in figure 4(d). This final configuration is 0.01 eV lower in energy than the previous one, and the energy barrier is also lowered to 0.94 eV, as shown in the right part of figure 4. Hence, after the first hydrogen has jumped, it is easier for a second hydrogen to do the same than for the first one to jump back. However, the lowest total energy is found in the latter situation showing that the pristine wire is more stable.

Alternatively, after the first hydrogen jumps it could diffuse along the wire, jumping to the next DB. Our calculations yield that this intrawall diffusion would decrease
the final total energy by 0.23 eV. After the pristine wire, the lower energy state corresponds then to a H atom that has diffused across the dimer and along the wire. The barrier associated with the intrarow diffusion is 1.44 eV. This result also shows that it would not be easy for a H atom to diffuse along a DB-wire. Even if an extra H atom is placed in the DB-wire coming from another source, the intrarow diffusion is large, amounting to 1.36 eV, similar in value to the previous intrarow diffusion barrier.

Experimentally, the reported values for intrarow diffusion barriers are about 1.68–1.98 eV [32–34]. These are ~0.2 eV higher than our computed value. Discrepancies are due to the different H coverage of the systems compared here. Indeed, thorough computations [35] with different H coverages yield a 0.25 eV difference between their computed high H coverage and low coverage limits.

In conclusion, for infinite DB-wires our stability studies show that the diffusion of hydrogen to the wire or along it is not a very favourable process, with associated energy barriers between 1 and 1.5 eV. Therefore a DB-wire can be considered as a quite stable structure when considering those lateral and on-line H surface diffusions.

4. Finite wires

In previous sections we have investigated the properties of infinite DB-wires, which can represent the properties of very extended wires. However, in practice we will deal with shorter DB wires in which finite-size effects can be important. Experimentally, Hitosugi et al [3] constructed wires ranging from 2 to 13 DB.

In order to investigate what are the properties of finite wires and how they change as their size increases, we have considered wires from 2 to 6 DB in a (4 × 8) unit cell. The results are summarized in figure 5, and compared with previous results from [11].

In general, we observe that the magnetic solutions are favoured for all the finite-size wires. The AFM solution is the most stable in all cases, although the NM-distorted case competes more in energy as the DB-wire length is increased. Even the FM case, which was less stable than the ideal case for the infinite wires, is preferred to the distorted case for the smaller cases, up to 3-DB in our SIESTA and VASP calculations, and up to 5-DB in the ones from [11]. In contrast to these results, Bird et al [9] find that a solution without spin polarization is the most stable for the 4-DB wire.

VASP and SIESTA methods give a similar behaviour, with the results shifted by almost a constant amount. This systematic discrepancy (less than 10 meV) is most likely due to the different treatment of the core electrons in both methods: PAW potentials [19] for VASP and norm-conserving pseudopotentials [24] for SIESTA.
In the upper panel of figure 5 a pronounced even–odd oscillation is found. It can be traced back to oscillations in the stability of NM-distorted wires. Their origin was assigned by Lee et al to the presence of a half-filled electronic state for the odd wires [11], which destabilize them compared to the even ones. Actually, in our calculations we observe that the NM-distorted solution for the odd wires is a local minimum only if the system is forced to be non-magnetic. If spin polarization is allowed, the NM-distorted solution is no longer stable and it evolves until converging to the AFM solution.

The results from Lee et al agree well with ours for the magnetic cases, but there is a discrepancy for the NM-distorted situations. Here, our VASP and SIESTA calculations predict a higher stability for the even-numbered wires, which make the even–odd oscillations in the upper panel of figure 5 more pronounced in our case. We assign this discrepancy to the need of a thorough atomic relaxation. Curiously enough, the agreement is better for the spurious NM-distorted solutions in the odd-numbered wires.

Due to the different number of atoms in the finite wires, even-numbered NM-distorted wires can have a lone Si atom in the second layer which plays the role of a soliton wall [10]. The average distortion increases as we increase the length of the wire, reaching its maximum for the infinite one. However, the convergence is fast, and for the 6-DB the values are very close to the infinite-wire ones. In the AFM configuration the values for the local magnetic moments are the same as the infinite case (0.50 $\mu_B$) except at the edges, where they increase to 0.56 $\mu_B$.

In general, we can conclude that, for the finite wires, the magnetic cases are more favourable than the distortion of the lattice, probably because of the increased electronic confinement of the system. Indeed the magnetic solutions are the only ones for wires with an odd number of DBs.

4.1. Finite-wire stability versus hydrogen diffusion

As we did for infinite DB wires, it is worth studying the stability of the finite ones. In this case we have started by studying the possibility of a H atom to intradimer diffuse in the 4-DB wire, as shown in the upper panels of figure 6. Our calculations show that, while the final situation is just slightly higher in energy (0.09 eV), the associated energy barrier is of 1.22 eV, similar to the cases studied in section 3.3.

Regarding the intrarow diffusion, when a H atom diffuses from the edge of the 4-DB wire to the inside, we obtain a barrier of 1.54 eV, also similar to the corresponding value for the infinite wire.

These results are in good agreement with previous calculations at different levels of H coverage on Si(001), where a systematic larger intrarow barrier is found compared to the intradimer one [32, 35]. Diffusion between rows is about one eV larger than the intrarow diffusion barrier [31, 32, 35] and we can effectively neglect it as a threat to the DB-wire stability.

Consequently, the finite wires can also be considered as stable, following this criterion.

5. Summary and conclusions

The present paper shows the properties of quasi 1D wires formed by lines of dangling-bonds (DB) created by the removal of H atoms from a monohydride Si(100) surface. In particular, emphasis is put on their stability and their capacity to be used in molecular-based devices.

The ideal infinite DB-wire presents a narrow metallic band and it is thus subjected to instabilities. Electron-vibration coupling opens a gap while inducing a Peierls distortion of the wire. Electron–electron interactions lead to different instabilities, in particular ferromagnetic and antiferromagnetic solutions that also open a band gap. Hence, realistic infinite DB wires are not metallic. According to our two calculations with different DFT-based methods, the ground state of the infinite wire corresponds to the Peierls distortion of the wire. Electron–electron interactions lead to different instabilities, in particular ferromagnetic and antiferromagnetic solutions that also open a band gap. Hence, realistic infinite DB wires are not metallic. According to our two calculations with different DFT-based methods, the ground state of the infinite wire corresponds to the Peierls solutions, with an important degree of geometrical relaxation.

Wires can be considerably perturbed if H atoms move away from neighbouring passivated bonds. Our computations show that the lower diffusion barriers correspond to intradimer diffusion, with the value of 1.47 eV in excellent agreement with experimental measurements [31]. Once a H has diffused into the wire, the barrier to diffuse a second neighbouring H atom goes down to 0.94 eV. Despite this reduction, the large activation barriers seem to guarantee the stability of DB wires.

Future atomic scale devices will rather include finite wires. Finite effects change the ground state of the wires from...
the non-magnetic distorted solution to the antiferromagnetic one. The short wires behave like molecular systems with discrete electronic levels that can be of great help in shaping the electronic transparency of those DB wires.

Finite wires have a larger number of neighbouring H atoms. But our study shows that the intrarow diffusion barrier is still very large in these systems (1.54 eV) and the bottleneck for H diffusion is the intradimer one. Hence, we expect DB wires to be stable against H contamination.

Given the robustness of these systems against other perturbations and contamination by neighbouring atoms, we expect short DB wires to gain importance in the creation of atomic scale devices [36].

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Figure 6. Reaction path for the intradimer diffusion of one hydrogen in the 4-DB wire, as shown in the upper panels. The colour code is the same as figure 1.
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