Diffusion of a polaron in dangling bond wires on Si(001)

LETTER TO THE EDITOR

Diffusion of a polaron in dangling bond wires on Si(001)

M Todorovic[1], A J Fisher and D R Bowler

Department of Physics and Astronomy, University College London, Gower Street,
London WC1E 6BT, UK

E-mail: andrew.fisher@ucl.ac.uk and david.bowler@ucl.ac.uk

Abstract
Injecting charge into dangling bond wires on Si(001) has been shown to induce
polarons, which are weakly coupled to the underlying bulk phonons. We present
elevated-temperature tight-binding molecular dynamics simulations designed
to obtain a diffusion barrier for the diffusive motion of these polarons. The
results indicate that diffusion of the polarons would be observable at room
temperature, and that the polarons remain localized even at high temperatures.

1. Introduction

There are many motivations to understand the transport properties of materials in the extreme
one-dimensional limit. Some are technological: the logical conclusion of the historic reduction
in size of electronic components would be device elements, and passive connections between
them, that are of atomic scale. There has been much recent interest in structures that might
act as such atomic-scale wires, or as atomic- or molecular-scale switches. Other reasons
relate to fundamental physics: transport in one dimension is qualitatively different from that
in higher dimensions, essentially because of the much stronger coupling that occurs between
the different possible excitations.

One particularly suitable system for the study of such effects, and also for potential
applications, is the dangling bond (DB) line on the Si(001) surface [1]. A local, highly
one-dimensional conducting channel is formed by the selective desorption of H atoms from
the hydrogenated surface, creating locally depassivated dangling bonds. Charge (produced
by injection or doping) may be expected to be strongly confined to the depassivated region.
Being an almost ideal one-dimensional conductor, this system shows features characteristic of
strongly coupled low-dimensional systems, including a Peierls-like Jahn–Teller distortion [2] in
which neighbouring depassivated Si atoms acquire alternating 'up' and 'down' displacements
normal to the surface.

[1] Present address: Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK.

It is tempting to draw an analogy with conjugated polymers, where a similar alternation occurs in the bond length [3]. In these systems, the coupling of injected charge to the bond alternation results in the formation of small polarons (charge carriers self-localized in the molecule by their own induced atomic distortions). Indeed, we have previously shown [4] that analogous excitations exist in the DB wires; our tight-binding calculations showed that a hole becomes localized on an 'up' atom, pulling it down (i.e. making it less sp^3-like), while an electron becomes localized on a 'down' atom, pulling it up (i.e. making it less sp^2-like). From this it is clear that there are important differences from, as well as similarities to, the conducting polymer case, because the predominant local chemistry driving the carrier localization involves a *single* atom.

It might be expected that the formation of polarons would have important consequences for the charge transport properties of the wire. It is already known that for conjugated molecular systems in the coherent limit, the charge transport becomes dominated by polaron tunnelling [5]. However, experiments on surfaces are more likely to operate in the incoherent limit; in this case, the most relevant quantity is the diffusion constant of the polaron along the DB chain. In this letter we address this issue by performing constant number of particles, volume and temperature (NVT) tight-binding molecular dynamics for diffusing hole polarons at a range of elevated temperatures. We choose hole, rather than electron, polarons because we believe our tight-binding calculation is likely to provide a better description (see section 2). The tight-binding approximation is important because it allows us to simulate large enough systems, and for long enough times, to gain useful information on the hopping. From the observed polaron hopping rates we are able to estimate the activation energy to hopping as only 0.06 eV. Our results show that the polaron is relatively mobile along the line, but confined perpendicular to it even at elevated temperatures.

The plan of the paper is therefore as follows. First, we describe the computational methods used. Then, we present results for the diffusional hopping rate, along with visualizations of the motion of the polaron and plots of the energy of the polaron state. We finish with a discussion of the results.

2. Computational details

The tight-binding technique has been reviewed elsewhere in detail [6]. We used a nearest-neighbour, orthogonal parametrization for Si–Si bonds and Si–H bonds designed specifically for the Si(001) surface [7] and tested extensively in this environment (in particular, it has been shown to reproduce *ab initio* simulations of the perfect, infinite DB wire rather well [4]). The simulations were performed with the OXON code, using exact diagonalization.

We used periodic boundary conditions, and simulated a surface with a slab geometry and a vacuum gap of 29 Å (the size is irrelevant in tight-binding simulations so long as it is greater than the hopping parameter cutoff). The unit cell was 12 dimers long and two dimer rows wide, with one dimer row completely covered with hydrogen and the other half-covered to yield the DB wire. There were six layers of silicon, the bottom of which was fixed in bulklike positions and terminated in hydrogen, giving a total of 420 atoms. Only the Γ-point of the reduced Brillouin zone was sampled.

The molecular dynamics simulations were performed at constant NVT, with the temperature maintained by a simple rescaling (if the temperature deviated by more than 1% the atomic velocities were rescaled to give the correct temperature). We used a timestep of 1 fs, and performed simulations for 1000 steps, giving a total time of 1 ps. The simulations were carried out at temperature intervals of 100 K beginning at 100 K and ending at 1000 K.

The starting point was a relaxed DB wire with a hole polaron already formed, illustrated in figure 1. The 'perfect' DB wire consists of a series of clean Si atoms along one dimer row
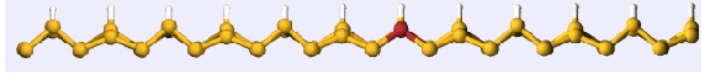
Figure 1. A hole polaron (marked as a darker atom) on a DB wire on Si(001).
(This figure is in colour only in the electronic version)

on a hydrogenated surface. As this would result in half-filled bands, the system is unstable towards a Peierls distortion [2, 8]. Alternate atoms in the wire are displaced up and down, with charge transferring from the down to the up atom. The hole polaron is then formed by displacing a single 'up' atom of the wire downwards normal to the surface to break the translational symmetry, and allowing the system to relax (with one fewer electron than required for charge neutrality). The structure and properties of the hole polaron (and the equivalent electron polaron) have been discussed elsewhere [4].

For the MD, the atoms were given random velocities corresponding to the appropriate Maxwell–Boltzmann distribution for the temperature being modelled, and after equilibration the system was allowed to evolve for 1 ps. As well as monitoring the standard parameters (such as different energies) we followed the weight of the contribution from each atom in the system to the top-most filled eigenstate, which is identified as the polaron state. This gives the location of the polaron with time, providing that it remains localized (for instance, in the relaxed polaron, this weight is ∼0.4 from the 'up' atom in the wire on which the polaron is located). A hop was defined to have occurred when the largest contribution changed from one atom to another. The occupation of the electronic states was weighted by the appropriate Fermi function at each temperature.

3. Results

Ten MD simulations were performed for each temperature as described above, and the number of hops at each temperature was used to give a hopping frequency (except at 100 K, where no hops were observed in any of the simulations). We assume an Arrhenius form for the hopping rate, p:

$$p = A\mathrm{e}^{-E_b/k_\mathrm{B}T}, \tag{1}$$

where E_b is the barrier to diffusion and A is the attempt frequency [9]. Then, by plotting the natural logarithm of the hopping rate against inverse temperature we should get a straight line. The gradient gives us the barrier to diffusion and the intercept the attempt frequency. The graph is shown in figure 2. The barrier is 0.06 eV and the attempt frequency 8×10^{13} s^{-1}.

On closer inspection, the graph seems to show a bend around 500 K; such behaviour has been seen for a small polaron before [10], but our model does not contain the necessary physics. The bend might also be caused by one or more alternative channels which open at high temperatures (as seen, for instance, for H in Nb [11, 12]). We also fitted a sum of two exponentials, i.e.

$$p = A_1\mathrm{e}^{-E_b^1/k_\mathrm{B}T} + A_2\mathrm{e}^{-E_b^2/k_\mathrm{B}T}. \tag{2}$$

Here, we find two sets of parameters: the attempt frequency and barrier for the first are 3×10^{13} s^{-1} and 0.043 eV; for the second, they are 2×10^{14} s^{-1} and 0.185 eV. This suggests that there may well be a number of competing channels to the diffusion at higher temperatures. Of course, at higher temperature the hydrogens also become mobile [13], though at these temperatures and timescales (i.e. over 1 ps) there is no hopping of the hydrogens. If we were
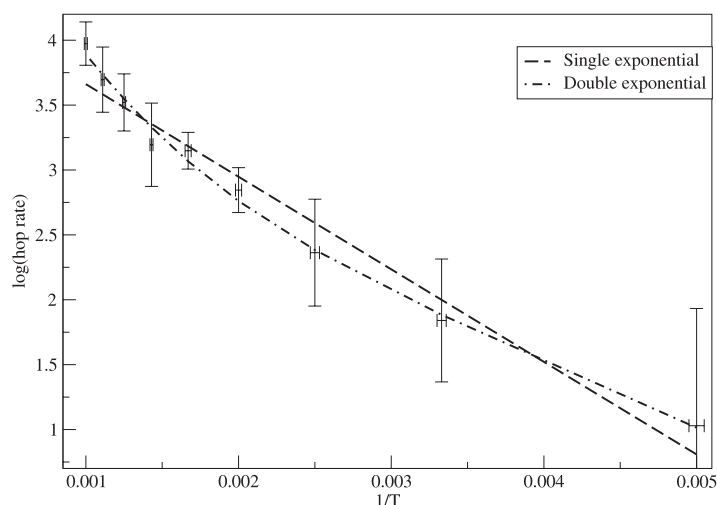
Figure 2. The log of the rate of hops plotted against inverse temperature. The dashed curve is a best fit to the data for a single exponential, while the dot–dashed curve is a best fit to the data for a sum of two exponentials.

to include the quantum effects alluded to above, this would be expected to further flatten the curve at low temperatures.

Since we output the contributions to the topmost filled eigenstate, we can follow the location and localization of the polaron at different temperatures. Interestingly, the polaron remains localized even up to high temperatures, and we can follow its location with time by plotting the location of any atom on which the weight is greater than 0.1. This is shown in figure 3 for individual runs at two temperatures: 200 and 700 K. The polaron moves around more at 700 K (as would be expected) but is still localized essentially on one atom, though there are times when it is shared between two or more atoms. This sharing is a prelude to a hopping attempt, and can also be seen for the 200 K case.

The transition state for the hopping of the polaron has proved difficult to isolate using tight binding. We have considered two ways of isolating it: first, mapping out a reaction pathway by constraining an appropriate reaction coordinate at various different values and relaxing the system at each of these points; second, analysing the MD results to extract the atomic motion around a hop. The first technique failed because of the ease with which charge can be transferred in tight binding. We chose as our start and end points the polaron localized on adjacent 'up' atoms, and constrained the height *difference* between these two atoms. Unfortunately, as we approached a difference of zero, the charge moved around (in particular moving to the hydrogenated ends of the dimers which were being constrained) and the structure distorted. We were unable to find a transition of the polaron from one 'up' atom to the next using this technique, though we believe that it was more due to the shortcomings of the tight binding. The second technique failed because the barrier is so small, and the thermal motion of the atoms was sufficient to conceal the details of the transition. We show this in two ways in figure 4. In figure 4(a), we plot the variation of the potential energy of the system throughout the run at 200 and 700 K; this shows that, even at 200 K, the energy was varying by far more than the 0.06 eV seen in the hopping of the polaron. In figure 4(b), we plot the energy of the top-most occupied state (which is also equivalent to the Fermi energy, because of the missing electron, and is the polaron state). From the plot, we can again see that the variation of the energy is
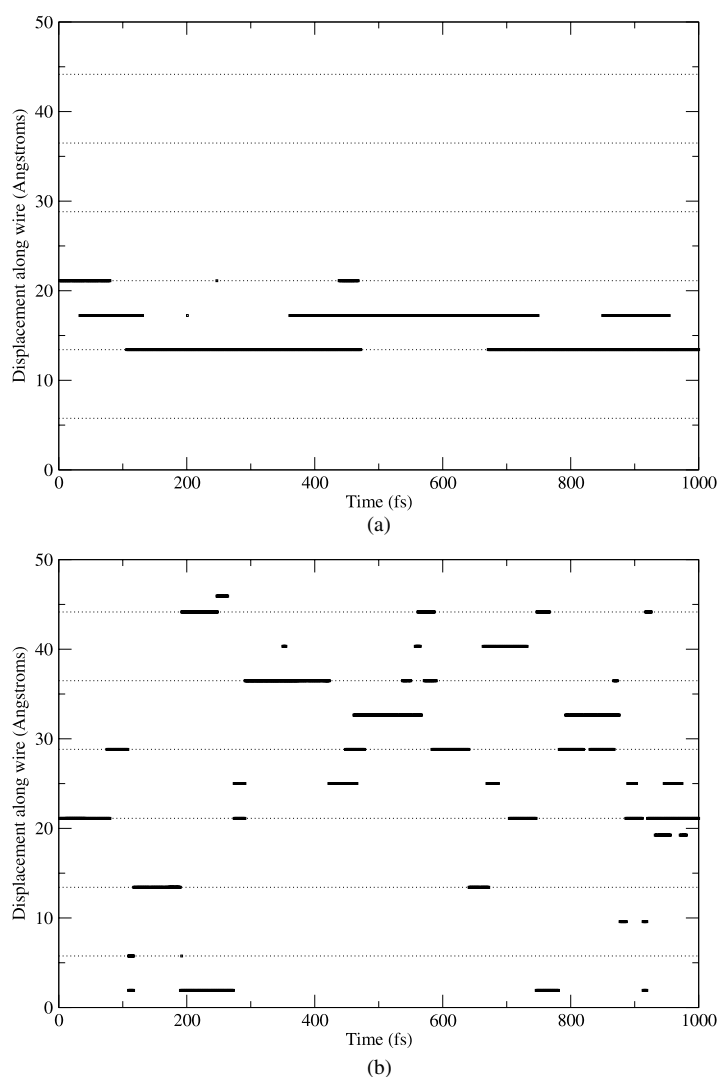
Figure 3. Displacement of the hole polaron along the DB wire as a function of time for (a) $T = 200$ K and (b) $T = 700$ K. Dashed lines across the page mark the location of the 'up' atoms in the DB wire and are separated by two atomic spacings or 7.68 Å.

larger, even for this state, than the hopping barrier. We have tried to correlate the peaks and troughs seen on this plot with the hopping events, but with limited success: there is a small correlation between the stationary points of the energy and hopping, but not sufficient to be of interest. This again is due to the random thermal motion—if we were able to follow the system for a sufficiently long time at low temperatures (say 50 K) we might learn more, but this would require prohibitively long MD runs.

4. Discussion and conclusions

Our results show that, despite the self-trapping, the charge carrier (hole in this case) is highly mobile on a timescale of 1 ps, even at 200 K. Importantly, however, it remains self-trapped—
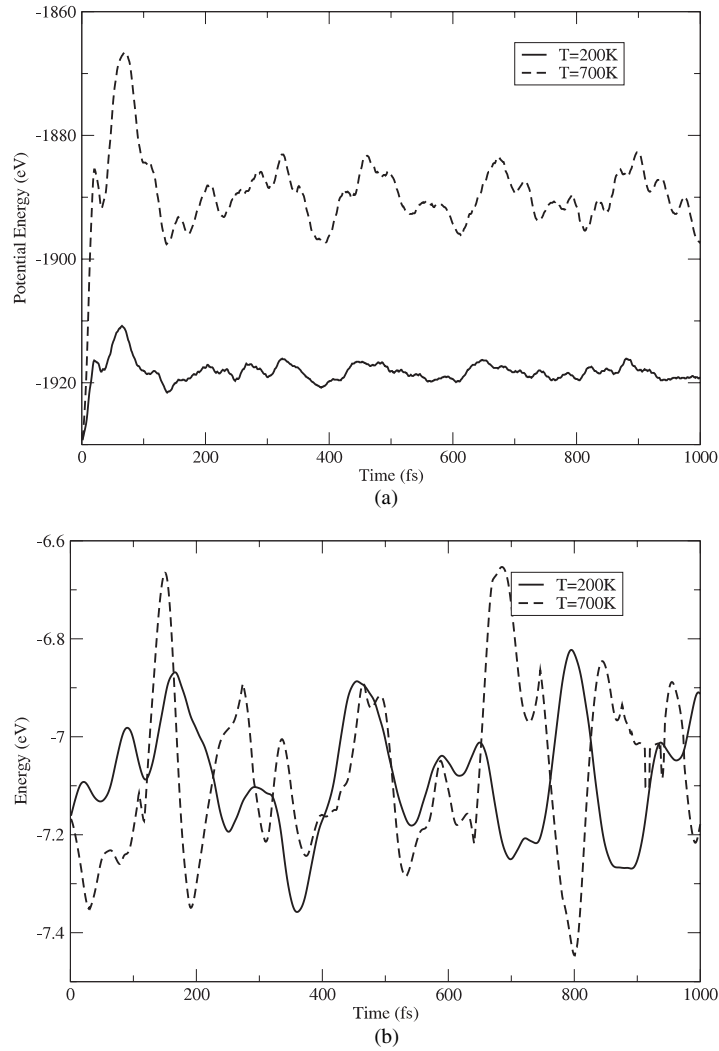
Figure 4. (a) Variation of potential energy with time for $T = 200$ K (solid curve) and $T = 700$ K (dashed curve). (b) Variation of energy of the top occupied eigenstate (equivalent to the Fermi level) with time for $T = 200$ K (solid curve) and $T = 700$ K (dashed curve).

and also localized on the DB wire. We expect that an electron polaron would have qualitatively similar properties. We can infer an effective diffusion constant and mobility from our data: the diffusion constant is $D = 2Ra^2$, where R is the hop rate (see figure 2), and a is the hopping distance of 3.84 Å. At 300 K, we find $D = 1.86 \times 10^{-6}$ m^2 s^{-1}. The mobility is found from the Einstein relation $\mu = eD/(k_B T)$; at 300 K we find $\mu = 7.19 \times 10^{-5}$ m^2 V^{-1} s^{-1}. Despite the self-trapping, this is an appreciable mobility.

It is important to ask how much effect our adoption of the tight-binding approximation had on these results. As explained previously, tight binding gives a good description of the neutral Peierls-distorted DB wire, reproducing both the band structure and geometry well. These factors between them should play a dominant role in determining the structure and mobility of the polaron, implying that, despite its simplicity, the tight-binding approach ought to describe the motion well.

In conclusion, we have shown that despite the predicted self-trapping, hole polarons in DB wires retain considerable mobility even at room temperature and below. This occurs through hopping between self-trapped configurations, with a barrier of 0.06 eV (assuming a single process) or 0.04 eV (at low temperatures, assuming competing processes). It is possible that the mobility might be further enhanced at low temperatures by quantum diffusion effects, not included in our calculations. Our calculations suggest that hopping at low temperatures may be slow enough to be observed directly in STM, provided that a mechanism for doping the wires can be devised.

References

[1] Shen T-C, Wang C, Abeln G C, Tucker J R, Lyding J W, Avouris Ph and Walkup R E 1995 *Science* **268** 1590
[2] Hitosugi T, Heike S, Onogi T, Hashizume T, Watanabe S, Li Z-Q, Ohno K, Kawazoe K, Hasegawa T and Kitazawa K 1999 *Phys. Rev. Lett.* **82** 4034
[3] Heeger A J, Kivelson S, Schrieffer J R and Su W-P 1988 *Rev. Mod. Phys.* **60** 781
[4] Bowler D R and Fisher A J 2001 *Phys. Rev.* B **63** 035310
[5] Ness H and Fisher A J 1999 *Phys. Rev. Lett.* **83** 452
[6] Goringe C M, Bowler D R and Hernández E 1997 *Rep. Prog. Phys.* **60** 1447
[7] Bowler D R, Fearn M, Goringe C M, Horsfield A P and Pettifor D G 1998 *J. Phys.: Condens. Matter* **10** 3719
[8] Peierls R E 1955 *Quantum Theory of Solids* (Oxford: Clarendon) p 110
[9] Vineyard G H 1957 *J. Phys. Chem. Solids* **3** 121
[10] Norgett M J and Stoneham A M 1973 *J. Phys. C: Solid State Phys.* **6** 238
[11] Gillan M J 1987 *Phys. Rev. Lett.* **58** 563
[12] Schober H R and Stoneham A M 1990 *Phys. Rev. Lett.* **60** 2307
[13] Bowler D R, Owen J H G, Goringe C M, Miki K and Briggs G A D 2000 *J. Phys.: Condens. Matter* **12** 7655