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Atomic-scale nanowires on Si(001): Cu on Bi

Alvaro Rodriguez-Prieto[1,2,*] and David R. Bowler[1,2,3,†]
[1]*London Centre for Nanotechnology, 17-19 Gordon Street, London WC1H 0AH, United Kingdom*
[2]*Thomas Young Centre@UCL, Gower Street, London WC1E 6BT, United Kingdom*
[3]*Department of Physics & Astronomy, UCL, Gower Street, London WC1E 6BT, United Kingdom*

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The fabrication of nanowires on the atomic scale is an extremely challenging process, typically only achieved via self-assembly or nanoscale lithography. We present density-functional theory results which show that a sequence of different nanowires one atom wide can be grown by deposition of copper on a nanoscale template: the Bi nanolines which self-assemble on Si(001). The resulting nanowires are characterized and show strong dispersion along the wire, as well as isolation from the substrate provided by the nanoline template.

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A change in dimensionality of a system often gives new physics: surfaces show completely different behavior to bulk material, often reconstructing, and one-dimensional metals have a very different behavior to two- or three-dimensional metals. Efforts to create one-dimensional wires[1] use systems such as carbon nanotubes,[2] directed assembly,[3] or self-assembly on stepped surfaces[4,5] with only partial control over the resulting structure or placement of the wires. While lithography at the atomic scale is possible,[6] it is prohibitively intensive and another route is needed. Nanoscale templating,[7–9] where a template is self-assembled and then overgrown with appropriate metals, is one promising route to formation of nanowires.

The integration of nanowires with semiconductor substrates has obvious technological applications. Semiconductor surfaces exhibit a large variety of reconstructions, and when a different material is deposited will often self-assemble into one- or two-dimensional structures. One example is the metastable nanowires formed by deposition of rare-earth metals[9] such as Er, Dy, Ho, and Gd. However, these nanowires exhibit a variety of widths (typically an odd number of surface unit cells) which makes their use as a template harder.

When a Bi-covered Si(001) surface is annealed around 600 °C, some of the Bi desorbs while the rest forms nanolines which are 1.5 nm wide, often over 1 μm long and atomically perfect (without kinks and generally without defects).[9] These nanolines have a larger band gap than the surrounding silicon surface[10] but are resistant to attack by low doses of radical hydrogen and oxygen,[11] which allows the substrate to be passivated. The Bi nanolines consist of pairs of Bi dimers on a complex subsurface reconstruction[12] (known as the haiku structure owing to its five- and seven-membered rings). This reconstruction involves considerable significant departure of the five layers beneath the Bi dimers from the diamond Si crystal, and has been predicted to offer stable binding sites for elements such as Mn and Fe.[13,14]

To date, experiments on overgrowth Bi nanolines with In (Refs. 15 and 16) and Ag (Ref. 8) have been reported. In alloys with the Bi dimers to form a one-dimensional, zigzag III-V chain which is not conducting; this wetting behavior is one limiting form of overgrowth. Ag forms well-separated islands which take on a series of heights which correspond roughly to layer separations in bulk; the resulting structures are not conducting though might offer intriguing routes to functionalization with organic molecules, for instance. We will show in this Rapid Communication that, despite its well-known tendency to be a fast diffuser in silicon, Cu deposition not only leads to segregation of Cu around the nanolines but also that the Cu inserts into the Si-Bi bonds to make conducting wires, which is a key goal of the research effort based on functionalizing and overgrowing nanoscale templates. Increasing coverage will lead to wires with different structures and properties, which we describe, allowing exploration of a family of atomic wires decoupled from the substrate.

Following our previous work,[17] we have used a plane-wave implementation of density-functional theory (DFT) within the local-density approximation, as implemented in the Vienna *ab initio* simulation package (VASP).[18] Ultrasoft pseudopotentials are used for all the elements considered. We use the haiku reconstruction in a computational cell containing one Bi nanoline on the Si (001) surface. In order to allow the haiku reconstruction to relax, the slab is formed of ten Si layers, whose two bottom layers have been fixed to their bulk positions and terminated with two H atoms each to mimic bulk conditions. In addition, the unit cell must be ten Si dimers long to allow sufficient strain relief. This restricts most calculations to a single dimer row wide, though we have made some calculations with two dimer rows when considering isolated Cu atoms bridging between rows (the D2 structure described below). Convergence of forces and energy differences is achieved with a Monkhorst-Pack mesh of $4\times2\times1$ for the single row cell (and $2\times2\times1$ for the two row cell) and an energy cutoff of 233 eV. Energy barriers have been calculated using the nudged elastic band method with a single image.[19]

Cu in silicon can be considered as a small, positively charged ion,[20] which is an extremely fast diffuser (with a diffusion barrier around 0.3 eV). It is well known for its detrimental effect on semiconductor devices.[21] We have recently examined its diffusion near a hydrogenated Si(001) surface,[17] and found that it follows a zigzag migration route along the dimer row direction;[17] there is a small but significant energy gradient which drives Cu toward the hydrogenated surface. Cu which is deposited on the surface will rapidly diffuse beneath the surface[17,22] but remain within the top two layers while any Cu outdiffusing from bulk will be chan-

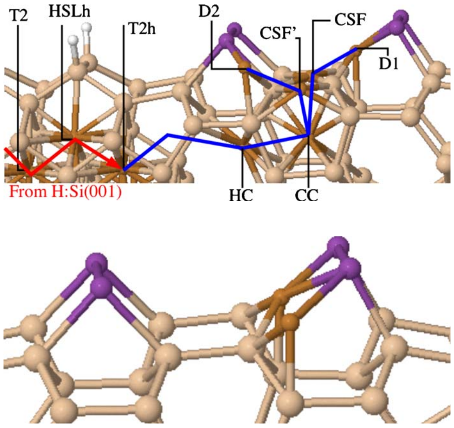

FIG. 1. (Color online) Top: binding sites and migration routes for Cu near Bi nanolines. Bottom: structure of D1D2 nanowire. H is colored white (lightest), Si beige (very light gray), Cu copper (light gray), and Bi purple (dark gray).

neled toward the surface, and along the dimer row. Our recent work[17] showed that individual Cu atoms on H:Si(001) has a barrier of 0.06 eV to diffusion subsurface, with barriers around 0.2 eV to diffusion beneath the surface; the third-layer interstitial site is the lowest energy position away from the nanolines.

The Bi nanolines self-assemble perpendicular to the dimer row so that Cu which is diffusing subsurface would encounter the reconstruction associated with the nanolines. We have modeled all possible diffusion barriers near the nanolines (which will be presented elsewhere[23]) and find that Cu atoms are attracted to the nanolines. Figure 1 shows the migration route which concerns this Rapid Communication, for Cu deposited from vacuum. Once it reaches the second-layer interstitial (T2h, binding energy −3.47 eV) nearest the nanoline it will move into the heptagonal cage under the Bi dimers (HC, −3.58 eV), diffusing through the pentagonal cage with an energy barrier of E_b=0.29 eV. Once at HC, Cu adatoms migrate to the central cage site (CC, −3.64 eV) with a very small barrier, E_b=0.05 eV. This suggests that Cu atoms can move essentially freely between HC and CC. From CC, Cu adatoms diffuse to one of two positions on the nanoline: the D1 (−3.72 eV) position or the D2 (−3.75 eV) position (illustrated in Fig. 1). The diffusion proceeds through either central square face sites (CSF, −3.53 eV, in line with the Bi dimers or CSF′, −3.50 eV, out of phase with the Bi dimers). While this requires a small rise in energy, the energy gain of the final positions is enough to drive the diffusion. The energy barriers are all between 0.39 and 0.54 eV [$E_b(\mathrm{CC}\rightarrow\mathrm{CSF})=0.47$ eV, $E_b(\mathrm{CSF}\rightarrow\mathrm{D1})=0.39$ eV, and $E_b(\mathrm{CSF}'\rightarrow\mathrm{D2})=0.47$ eV followed by $E_b(\mathrm{CC}\rightarrow\mathrm{CSF}')=0.54$ eV or equivalent paths from CC′ → CSF′].

Several of these barriers are larger than the subsurface diffusion barrier so we must consider carefully what happens to Cu near the haiku reconstruction. The driving force will be the energetic gain near the Bi nanolines—from T2h to CC there is a gain in energy of 0.17 eV making the barrier to leave the nanolines 0.46 eV. This is close to the barrier to go on from CC to CSF (or CC′ to CSF′). Thus once a Cu atom arrives at CC it has at least a 50% chance of moving on to a site from where it can decorate the Bi nanoline.

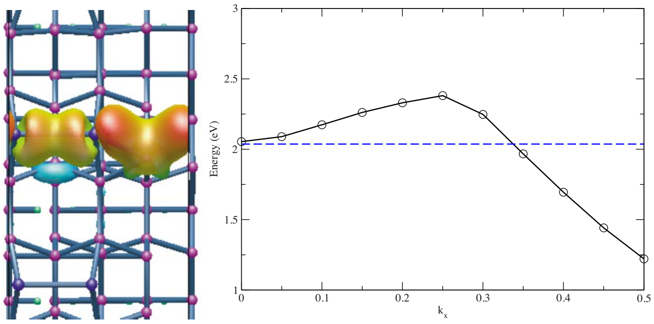

FIG. 2. (Color online) Electronic structure of the D2 wire. (Left) Charge-density isosurface for VBM. (Right) Dispersion along the wire (i.e., in x direction) for VBM.

While we find that the D2 position is marginally the lowest energy position, it is equivalent to an infinite wire of D2 copper atoms (in a single dimer row cell, the D2 bridges between Bi dimers in the unit cell and its images). We have checked the relative stability of isolated and extended D2 sites by calculating the energy of an isolated D2 in the two dimer row cell, as well as comparing an infinite D2 nanowire in the two dimer row cell with an isolated D1D2 unit. The infinite D2 wire is 0.3 eV more stable per Cu than the isolated D2 Cu; however, the isolated D1D2 Cu pair and the D1D2 infinite Cu nanowire are very close in energy to the D2 nanowire, with the infinite D1D2 marginally more stable. This stabilization will not occur for the D1 site, which does not bridge between Bi dimers. It is important to note that this tendency to form linear structures rather than clusters is in direct opposition to Ag which forms nanoislands on the nanolines.[8]

The simplest nanowire, and the first to form, is therefore the infinite D2 wire, and we consider its properties first. The partially occupied valence-band maximum (VBM) of the D2 wire extends across the dimer rows, and is decoupled from the substrate, as illustrated in Fig. 2. This state shows strong dispersion along the wire, also shown in Fig. 2 with close to quadratic behavior from the middle of the zone toward the edge of the zone. Doubling the unit cell along the wire (so that there are two Cu atoms, both in D2 positions) has no quantitative effect on the band structure, leading to the same dispersion and no distortion effects as are common on semiconductor surfaces; specifically, there is no Peierls distortion and the addition of spin polarization does not lead to a quantitative change in the bands or electronic structure. The D2 nanowire is the structure which we believe is most likely to show the interesting physics associated with one-dimensional systems.

An important question to consider is how the addition of further Cu will affect the structure (and hence properties) of the nanowires. Calculating the binding energies of Cu in different positions, as well as barriers between the most stable of these positions, certainly gives guidelines for how the development will proceed. Crucially, we find that filling in gaps in the D2 nanowire to give a D1D2 nanowire, followed by the creation of new nanolines (there being two sites for a D1D2 nanowire in each Bi nanoline) is favored over cluster-

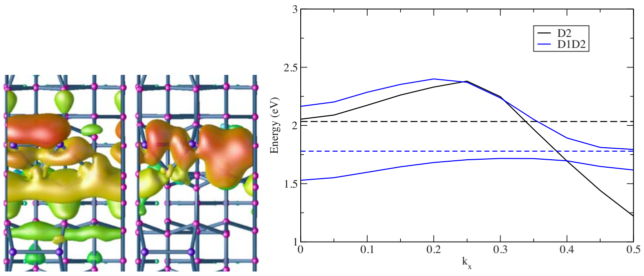

FIG. 3. (Color online) Electronic structure of the D1D2 wire. (Left) Isosurfaces for VBM and CBM; color (grayscale) indicates height. (Right) The dispersion behavior along the nanowire (*x* direction) for the VBM and CBM for the D1D2 nanowire [blue (light gray) lines] and the VBM for the D2 nanowire (black lines). The Fermi levels are indicated by dashed lines in blue (light gray) (D1D2) and black (D2).

ing: this is a key difference to the measured and calculated behavior for Ag.

We must also consider the possibility that a D2 wire will not be the first to form on any given Bi nanoline, with a D1 wire formed instead. This structure does not have metallic properties, in particular, because there is no link between adjacent Bi dimers. A Cu bonded at the D1 position affects only one Bi dimer while a Cu in the D2 position inserts into the backbonds of neighboring Bi dimers giving both linkage between Bi dimers and hence metallic behavior and a strong energetic reason to extend the line (once one backbond has been opened, the energy to add another Cu at an adjacent D2 position is lower). The barriers as well as binding energies are reduced, when both D2 and D1 Cu atoms are present. For instance, once a Cu is at D2, the barrier to D1 from CSF is reduced from 0.39 to 0.29 eV. Similarly, the energy barrier from CSF′ to D2 is decreased by the presence of a Cu at the D1 site. The resulting D1D2 configuration is slightly energetically favored over either D1 or D2 configurations alone, which will lead eventually to the formation of a D1D2 nanowire.

The electronic structure of the D1D2 nanowire is similar to the D2 nanowire, showing a VBM which is delocalized along the Bi nanoline and decoupled from the substrate. This is plotted in Fig. 3. With two Cu atoms in each unit cell, there are now two electrons, which leads to a filled band at the VBM, though this still shows strong dispersion and a very small band gap.[24] The dispersion of the bands are also plotted in Fig. 3, with the D2 nanowire shown to provide contrast. Again, the delocalization produced by the Cu atoms linking Bi dimers leads to strong dispersion in the CBM which suggests interesting properties of this wire.

We can understand something of the changes caused by Cu insertion into the Bi nanolines by looking at the local density of states[25] on the atoms, as shown in Fig. 4. Comparing the Bi atoms in the clean dimer (which have a DOS which is essentially identical to the Bi atoms in dimers on a clean haiku reconstruction) to the Bi bonded to Cu in the D2 nanowire, we see that a strong feature is introduced into the gap, which is partly occupied as shown by the bands plotted in Fig. 2; it is also interesting that the DOS of the Cu and Bi are closely correlated around the Fermi level (further from the Fermi level, they differ significantly as might be expected). The Bi and Cu atoms in the D1D2 nanowire also show a feature in the gap, but with a small splitting, in good agreement with the bands in Fig. 3. In both cases, the insertion of Cu into the Bi-Si bonds has introduced electronic states near the center of the gap while leaving the neighboring Bi dimers almost unaffected.

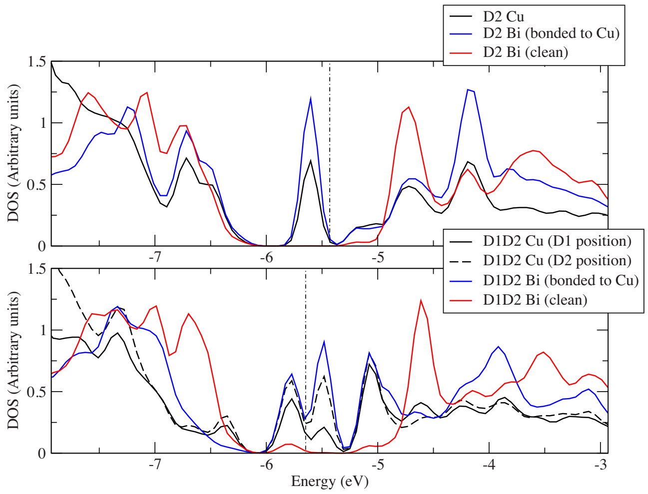

FIG. 4. (Color online) Density of states for Cu and Bi atoms in the D2 nanowire (above) and D1D2 nanowire (below). The Fermi level is shown by a vertical dotted-dashed line in both cases, and the DOS are aligned to absolute Kohn-Sham eigenstate energies.

Adding further Cu atoms will lead to a saturation of the Bi nanolines, with the D1D2D1D2 configuration (consisting of a D1D2 nanowire in each set of Bi dimers on a given nanowire) emerging as the most favored structure. This consists of two parallel D1D2 atomic wires, with Cu inserted in all internal backbonds of the Bi dimers. The electronic properties of the D1D2D1D2 nanowires are little changed compared to the D1D2 nanowires.

The formation of the nanowires is likely to proceed as follows. Assuming that Cu is deposited from the vacuum, it will move subsurface and migrate rapidly toward the Bi nanolines. Once in their vicinity, we have described the path whereby Cu atoms will reach the CC site in the center of the nanoline. A Cu atom is slightly more likely to migrate to a D2 site, though this is a very marginal assignment. Once a D2 or D1 nanowire has nucleated, however, it will rapidly lengthen; we suggest, therefore, that a very low dose of Cu is likely to lead to at least a 50% population of D2 nanowires, which are predicted to be very interesting structures. Extremely low doses of Cu will be necessary to create these nanowires. We note that there is an energy gradient which will keep Cu near the surface of the H-terminated Si(001), and an immediate gain of ~0.2 eV when Cu moves from the T2 to the CC site, which will offset any entropic tendency to distribute the Cu through the bulk crystal.

Addition of further Cu will bias the system toward denser nanowires, forming the D1D2 structure. While these will not be quite as promising metallic nanowires as the D2 wires, they nevertheless show a delocalized electronic structure along the wire and dispersion effects. For Cu doses up to the surface Bi density, we believe that elongated nanowires following the Bi nanolines should result. Beyond this dosage, we make no predictions, though note that the subsurface sites around the nanoline are low in energy for Cu atoms, and that subsurface Cu nanowires might result.

We have presented calculations for Cu on a hydrogen-terminated Si(001) surface in which Bi nanolines have been grown. We have shown that Cu will diffuse to the nanolines (via a subsurface route) and form atomic wires by inserting into the backbonds of the Bi dimers; the Cu will be confined in the vicinity of the Bi nanolines. Unlike Ag, which aggregates into islands on the Bi nanolines, the Cu shows a strong tendency to form extended wires. The addition of more Cu to existing wires will increase the density of Cu in the wires, up to a coverage equivalent to the Bi surface coverage. We have not modeled the stability of Cu in the nanolines beyond this coverage but we note the presence of a number of stable sites below the surface (the two heptagonal cages as well central cage) which will certainly attract any Cu which does not bind to the surface. The ability of Cu to diffuse beneath the surface, which Ag does not do, will allow the subsurface haiku reconstruction to act as a sink.

The resulting Cu nanowires show properties which depend on the coverage but should broadly be conducting. The D2 nanowire, with a single Cu atom in the unit cell, shows the most interesting dispersion but all the nanowires have a VBM which is extended and decoupled from the substrate. A careful experimental study of deposition and annealing of Cu on Bi nanolines in H:Si(001) should provide methods for fabricating genuinely atomic-scale nanowires which are well decoupled from the substrate.

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*Present address: Tecnalia Construcción, Grupo NANOC, Fundación Labein Tecnália, Parque Tecnológico de Bizkaia, Edificio 700, c/Geldo, 48160 Derio, Bizkaia, Pais Vasco, Spain.

†david.bowler@ucl.ac.uk

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[24] DFT underestimates band gaps significantly; however, the gap for the D1D2 nanowire is much smaller than the substrate or surface so that there will likely be significant conductivity given doping or thermal excitation.

[25] We projected the Kohn-Sham states onto spheres of radii 1.5, 1.8, and 1.5 Å for Cu, Bi, and Si to plot the DOS.