Surface structure of cubic diamond nanowires

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Abstract

Presented are results of our ab initio study of the surface reconstruction and relaxation of (100) surfaces on diamond nanowires. We have used a density function theory within the generalized-gradient approximation using the Vienna ab initio simulation package, to consider dehydrogenated and hydrogenated surfaces. Edges of nanowires offer a new challenge in the determination of surface structure. We have applied the methodology for stepped diamond (100) surfaces to this problem, and consider it useful in describing diamond nanowire edges to first approximation. We have found that dimer lengths and atomic layer depths of the C(100)(2×1) and C(100)(2×1):H nanowire surfaces differ slightly from those of bulk diamond and nanodiamond surfaces. The aim of this study is provide a better understanding of the effects of nano-scale surfaces on the stability of diamond nanostructures.

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1. Introduction

The emerging field of molecular nanotechnology has introduced a wide range potential applications of nanostructured materials, for a variety of purposes. One-dimensional (1-D) nanowires have been proposed as important components, playing an integral part in the design and construction of both electronic and optoelectronic nanodevices [1]. Significant work has been compiled regarding the structure and properties of semiconductor nanowires including silicon [2,3], silicon carbide [4,5] and carbon [6]. The growth of carbon nanowires has been achieved using a number of techniques including laser-induced chemical vapor deposition [7], high pressure treatment of catalyst containing thin films [8], annealing of silicon carbide films [9] and annealing of pressed graphite containing tablets [10]. Aligned diamond nanowhiskers (a term used to describe particular nanowires) have been formed using air plasma etching of polycrystalline diamond films [11]. Dry etching of the diamond films with molybdenum deposits created well-aligned uniformly dispersed nanowhiskers up to 60 nm in diameter with a population density of 50/μm². These diamond nanowhiskers showed well-defined characteristics of diamond [12].

Diamond (carbon) based materials have been suggested to be the optimal choice for nanomechanical designs, due to their high elastic modulus and strength-to-weight ratio [13,14]. This has prompted a number of theoretical studies investigating various aspect of diamond at the nano-
An important aspect of simulating nanodiamond structures is to correctly model their surfaces. Clean [15–20] and hydrogen passivated [16–28] C(100) bulk diamond surfaces have been the topic of many investigations using a variety of experimental and theoretical methods. More recently the (100) surfaces of diamond nanocrystals have been examined [29,30]. To assist in providing a better understanding of the surfaces of diamond nanostructures we are interested in extending these research efforts to include diamond nanowires.

Presented here is a density functional theory (DFT) study of the surface structure of selected diamond nanowires using the Vienna ab initio simulation package (VASP) [31,32]. We used ultra soft, gradient corrected Vanderbilt type pseudopotentials [33] as supplied by Kresse and Hafner [34], and the valence orbitals are expanded on a plane-wave basis up to a kinetic energy cutoff of 290.00 eV. All calculations were performed in the framework of DFT within the generalized-gradient approximation (GGA), with the exchange-correlation functional of Perdew and Wang [35]. This method has been successfully applied to bulk diamond [36] and nanodiamond [37], and has been shown to give results in excellent agreement with experiment and all electron methods [26].

The surface structure has been analysed for two dehydrogenated and two hydrogenated diamond nanowires with cubic morphology. To ensure that the structures are close to equilibrium, both the ions and super-cell volume were structurally relaxed. Both the symmetry and the lattice parameter of the nanowires were free to vary, resulting in expansions or contractions of the entire structures. The relaxations were performed for a minimum of 20 ionic steps (involving changes in the atomic positions), each initially consisting of approximately 50–60 electronic steps (involving changes in the electronic charge density surrounding the atoms) and converging to a minimum of 3 electronic steps during the final ionic steps.

2. Diamond nanowires

Four infinite diamond nanowires were included in this study, consisting of dehydrogenated and monohydrogenated versions of two cubic structures. The structures are periodic along a [1 1 0] direction, with two C(1 0 0)(1 × 1) surfaces and two C(1 1 0)(1 × 1) surfaces along the length of the nanowire. The length of the simulation cell was \( \sim 1.5 \) nm, creating (periodic) nanowire segments with two distinct rectangular cross-sections. The smaller segment has an average lateral diameter of 0.6 nm and contains 132 carbon atoms in the simulation length, while the larger segment has an average lateral diameter of 0.85 nm and contains 240 carbon atoms in the simulation length. The hydrogenated segments consisted of \( \text{C}_{132}\text{H}_{72} \) and \( \text{C}_{240}\text{H}_{96} \) respectively. While the cross-section considered here represents only a simple case (that may not be currently realistic), it has been chosen as it facilitates the consideration of edges as well as generous surface facets. The finite size of nanostructures, such as nanodiamond and diamond nanowires, lead to ‘full structure’ relaxation that affect the surface as well as the bulk-like core of these systems [29]. It is considered important to begin to understand the variations in the structure of diamond nanowires effected by various finite size effects (beginning with a simple case), because at the nanoscale the surface structure plays a significant role in the electronic properties of the nanowire as a whole.

In all cases the initial step of the relaxation involved the reconstruction of the C(100) surfaces to form the (2 × 1) surface structure. As the C(110) surface does not reconstruct [38], the reconstruction is limited to the C(100) surfaces under consideration. The initial and final (relaxed) structures of the smaller dehydrogenated nanowire are shown in Fig. 1, and final monohydrogenated version in Fig. 2. Figs. 3 and 4 show the dehydrogenated and monohydrogenated results for the larger nanowire, respectively. Each nanowire is shown from the [100] direction (left), [110] direction (centre), with the periodic boundaries to the left and right of each image; and along the axis of the nanowire (right).

In the case of the larger nanowires, the characterization of the C(100)(2×1) surfaces was achieved by considering the difference in the primary \( d_{11} \) and secondary \( d_{12} \) dimer lengths, and the first \( Z_{12} \) and second \( Z_{23} \) layer depths. A diagram
outlining this nomenclature is given in Fig. 5. Examination of the structures shown in Figs. 1–4 reveals that there are two distinct (100) surfaces, with dimer rows running parallel and perpendic-
ular to the nanowire axis. These have been denoted C(100)\(\perp\) and C(100)\(\parallel\) respectively, and are shown explicitly in Fig. 6. The surface properties of each of these surface types has been determined for dimers positioned at the nanowire edges, and dimer positions in the centre of the nanowire (100) facets.

Inspection of Table 1 reveals that the dehydrogenated surface reconstruction and relaxation varies depending upon the region of the nanowire face in both the C(100)\(\parallel\) and C(100)\(\perp\) cases. The primary \(d_{11}\) dimer length is reasonably sensitive to region of the surface, and the \(d_{12}\) dimer length is consistently shorter at the edges than the centre of the facets (although this is more pronounced for the C(100)\(\perp\) surface). The \(Z_{12}\) depth is also smaller for dimers situated at the nanowire edges, than those at centre. The \(Z_{23}\) depth is significantly reduced at the edge of the C(100)\(\perp\) face being only 0.67 Å, closer to a \(Z_{12}\) depth than the bulk diamond layer separation of 0.89 Å. Overall the C(100)\(\parallel\) surface with dimer rows parallel to the nanowire axis shows little variation over the surface, although a slightly concave surface has resulted (indicated by the difference in the \(Z_{12}\) depth for the edges and surface centre). This concave relaxation is evident when viewing the nanowire along the axis, as in the lower right image of Fig. 3.

Saturation of the nanodiamond surfaces with hydrogen produces structures of lower energy that is entirely due to the passivation of surface bonds. However, aside from this, Table 1 shows that monohydrogenation of the nanowire surfaces has an important effect on the surface structure. The addition of the hydrogens removes much of the variation in surface structure over the (100) faces. The \(d_{11}\) and \(d_{12}\) dimer lengths and the \(Z_{12}\) and \(Z_{23}\)
layer depths are similar but not identical for the edges and centres of the C(100) faces (see Table 1).

In addition to the surface reconstruction and relaxation, the nanowires were also found to undergo full-crystal relaxations. Both the average lateral diameter and the simulation length was found to contract, although this effect was significantly reduced by surface hydrogenation. These relaxations contribute to the relaxations of the surfaces, and have an impact on the final surface structure. No bucking or twisting of the surface dimers could be discerned due to the edge effects.

3. Discussion: comparison with bulk and nanodiamond

Ignoring for a moment the variations in surface structure over the (100) facets, the average primary and secondary dimer lengths and average first and second layer depths (for the dehydrogenated and monohydrogenated cases) have been compared with bulk diamond and nanodiamond (see Table 2).

The results of the dehydrogenated surfaces show that the average $d_{11}$ and $d_{12}$ dimer lengths and the $Z_{12}$ and $Z_{23}$ layer depths for diamond nanowires falls between those of nanodiamond crystals and bulk diamond surfaces. For the monohydrogenated surfaces, the average $d_{11}$ and $d_{12}$ dimer lengths and the $Z_{12}$ and $Z_{23}$ layer depths for diamond nanowires are larger than those of both bulk and nanodiamond. This surprising result is most significant in the case of the $d_{11}$ dimer length and $Z_{23}$ layer depth, both of which are ~0.05 Å larger that those of bulk diamond.

However, as shown above, edges of the nanowires cannot be ignored. Using the nomenclature

Table 2

Comparison of average nanowire C(100) surface properties with bulk and nanodiamond

<table>
<thead>
<tr>
<th>C(100)</th>
<th>Bulk diamond</th>
<th>Diamond nanocrystals</th>
<th>Diamond nanowires</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{11}$ (Å)</td>
<td>1.385±0.003</td>
<td>1.44±0.06</td>
<td>1.405±0.002</td>
</tr>
<tr>
<td>$d_{12}$ (Å)</td>
<td>1.517±0.006</td>
<td>1.49±0.08</td>
<td>1.50±0.02</td>
</tr>
<tr>
<td>$Z_{12}$ (Å)</td>
<td>0.68±0.08</td>
<td>0.59±0.07</td>
<td>0.66±0.02</td>
</tr>
<tr>
<td>$Z_{23}$ (Å)</td>
<td>0.91±0.08</td>
<td>0.80±0.12</td>
<td>0.90±0.15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C(100):H</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>$d_{11}$ (Å)</td>
<td>1.632±0.008</td>
<td>1.63±0.02</td>
<td>1.681±0.008</td>
</tr>
<tr>
<td>$d_{12}$ (Å)</td>
<td>1.545±0.005</td>
<td>1.54±0.04</td>
<td>1.55±0.01</td>
</tr>
<tr>
<td>$Z_{12}$ (Å)</td>
<td>0.81±0.06</td>
<td>0.82±0.04</td>
<td>0.86±0.02</td>
</tr>
<tr>
<td>$Z_{23}$ (Å)</td>
<td>0.91±0.09</td>
<td>0.83±0.07</td>
<td>0.92±0.07</td>
</tr>
</tbody>
</table>

The nanowire results are averaged over the ‘edge’ and ‘centre’ regions.
of Chadi [39] single-atom steps on diamond (1 0 0) surfaces are denoted as $S_A$ and $S_B$ when the direction of the upper terrace (2 × 1) dimers are oriented perpendicular to the step edge and parallel to the step edge respectively. Further, $S_A$ type steps may be denoted as $S_B(n)$ for the non-bonded type, where there are no re-bonded atoms on the lower terrace; and $S_B(b)$ for the bonded type which does have re-bonded atoms on the lower terrace. Therefore, if we consider the edges of the nanowires as exaggerated steps, then the structure of the edges of the C(1 0 0)|| represent $S_A$ steps, and the edges of the C(1 0 0)⟂ represent $S_B(n)$ steps. Under this assumption, the $d_{11}$ dimer lengths for these step types (given in Table 1), may be compared with the results for stepped bulk diamond (1 0 0) surfaces.

Calculations by Alfonso et al. [40] using DFT LDA molecular dynamics determined that for the dehydrogenated surface the symmetric, unbuckled sp$^2$ hybridized $S_A$ step had a $d_{11}$ dimer length of 1.37 Å. Similarly, the symmetric sp$^2$ hybridized $S_B$ step had upper terrace $d_{11}$ dimer lengths of $\sim$1.48 Å. In the case of the monohydrogenated stepped surface, the $S_A$ step had a $d_{11}$ dimer length of 1.61 Å.

Although the dehydrogenated surfaces compared reasonably well with the corresponding stepped diamond surfaces, the monohydrogenated nanowire surfaces did not. The C(1 0 0)|| $d_{11}$ length for the dehydrogenated diamond nanowire edge was found to be 0.014 Å greater than the $S_A$ step on a bulk surface. However, the C(1 0 0)⟂ surface with dimers rows perpendicular to the nanowire axis shows more significant differences between the nanowire edges and facet centres. The $d_{11}$ length at the edge was found to be 0.02 Å less than the $S_B(n)$ step on a bulk surface. In the monohydrogenated case, the $d_{11}$ dimer length of 1.701 Å for the nanowire C(1 0 0)|| edge is 0.091 Å greater than 1.61 Å for the $S_A$ bulk diamond step [40]. It is also 0.081 Å greater than $S_A$ step results of 1.62 Å determined using the hybrid Density Functional (LDA) Tight-Binding (DF-TB) molecular dynamics study by Skokov et al. [24]. In contrast, the calculated $d_{11}$ dimer length of 1.657 Å for the monohydrogenated nanowire C(1 0 0)⟂ edge is only 0.027 Å greater than 1.63 Å for $S_B$ type steps [24].

In summary, the dehydrogenated C(1 0 0)|| $d_{11}$ length is closer to the bulk diamond $S_A$ step, whereas the monohydrogenated C(1 0 0)⟂ $d_{11}$ length is closer to the bulk diamond $S_B(n)$ step. This suggests that to improve surface homogeneity dehydrogenated diamond nanowires should be constructed with C(1 0 0)(2 × 1) dimer rows parallel to the nanowire axis, but monohydrogenated nanowires with dimer rows perpendicular to the nanowire axis.

4. Conclusion

The results outlined here show that although a considerably degree of localized variation in surface structure exists due to the nanowire edges, hydrogenation of diamond nanowire C(1 0 0) surfaces reduces these variations. Averaging over the variations, the structure of dehydrogenated cubic surfaces on diamond nanowires are characterized by features in between bulk and nanodiamond cubic surfaces. In contrast however, the feature of monohydrogenated cubic nanowire surfaces do not fall between bulk and nanodiamond. All of the considered features, including dimer lengths and atomic layer depths, exceeding those of bulk and nanodiamond. This highlights that ‘full structure’ relaxations are significant, and must be taken into consideration when studying the structure of surfaces at the nanoscale. Simply scaling the surface properties, or making assumptions regarding surface structure that do not include finite size effects is inappropriate.

By comparing results for surfaces with dimer rows oriented both parallel and perpendicular to the nanowire axis, it has been determined that dehydrogenated diamond nanowires should ideally be constructed with C(1 0 0)(2 × 1) dimer rows parallel to the nanowire axis, but monohydrogenated nanowires with dimer rows perpendicular to the nanowire axis. It is considered that these dimer arrangements will improve surface homogeneity and promote bulk-diamond-like surface features in each case.

Acknowledgements

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References