Effect of surface energy on the growth of boron nanocrystals

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Abstract. The surface energies of α-rhombohedral (α-rh), β-rhombohedral (β-rh), α-tetragonal (α-t), and β-tetragonal (β-t) boron were calculated from first principles to investigate their role in nano-scale crystal growth. Equilibrium shapes of boron crystals were obtained using Wulff’s theorem. Our results show that α-t boron, despite its low cohesive energy, is more stable than the other structures as a result of its low surface energy when the number of atoms is less than about 216. Since the nanowire of α-t boron that was obtained experimentally was larger than this, it was probably in a metastable state. The difference between the surface energy of the ab-plane and that of the ac-plane explains why the α-t nanowires grow in the c direction.

1. Introduction

Boron is an element in Group IIIB, and is generally a semiconductive material with covalent bonds. Whereas boron forms compounds that have a variety of structures, elemental boron itself has mainly four polymorphs: α-rhombohedral (α-rh), β-rhombohedral (β-rh), α-tetragonal (α-t), and β-tetragonal (β-t). Of these, α-rh and β-rh boron have been well studied because they are fairly stable and easy to synthesize. α-rh boron is believed to be the most stable at low temperatures. It transforms into β-rh boron at about 1400 K [1]. α-t and β-t boron are less studied than α-rh and β-rh boron.

The synthesis of α-t boron was first reported in 1943 by Laubengayer et al. [2] and later its structure was precisely determined as B$_{50}$ by Hoard et al. [3]. However, in 1971, studies by Amberger et al. concluded that pure α-t boron could not be synthesized in the absence of carbon or nitrogen as an impurity [4-6]. These studies asserted that what was assumed to be α-t boron was actually B$_{50}$C$_2$ or B$_{50}$N$_2$ and the structures of these compounds were proposed. In 1992, Lee et al. [7] showed by first-principles calculations that α-t boron could be made more stable by the inclusion of carbon, and along with their calculations of lattice parameters, they concluded that the α-t boron obtained by Hoard et al. [3] was probably B$_{50}$C$_2$. It is now thought that α-t boron does not exist in pure form.

Nevertheless, we believe that this assertion is not fully confirmed. First, the original synthesis experiments [2-6] were conducted using chemical vapor deposition (CVD), and it is not known what will happen if other methods are applied. Second, the work by Lee et al. [7] indicates only that B$_{50}$C$_2$ is more stable than pure B$_{50}$, and does not directly disprove the existence of B$_{50}$.

Since 2001, the synthesis of wire-like structures from boron has been reported [8-15], with some structures adopting α-t structures [11, 12, 14, 15] (table 1). These are called nanowires [11, 14], nanobelts [12], or nanoribbons [15]. For the sake of simplicity, the term “nanowire” will be used throughout this paper to refer to these structures. Yang et al. [14] and Xu et al. [15] reported that α-t nanowires contain impurities, a view that is consistent with the earlier results. Zhang et al. [11], on the other hand, suggested that the α-t nanowire that they produced consisted solely of boron atoms, and...
Wang et al [12] insisted that they did not observe any impurities in their nanowire. These two groups used the laser ablation (LA) method to create the nanowires, whereas CVD was used in the other preparations. If pure α-t boron actually exists, this is a significant result, since it has long been regarded as an impossibility.

Table 1. Experimental and calculated lattice constants of α-tetragonal boron. LA: laser ablation, CVD: chemical vapor deposition.

| a (Å)  | c (Å)  | synthesis method | impurities | reference |
|--------|--------|------------------|------------|-----------|
| 8.84   | 5.00   | LA without catalyst | undetected | Wang et al [12] |
| 8.75   | 5.06   | LA with catalyst | undetected | Zhang et al [11] |
| 8.73   | 5.03   | CVD | C, Cu | Yang et al [14] |
| 8.79   | 5.09   | CVD | C, O | Xu et al [15] |
| 8.75   | 5.06   | CVD | not available | Hoard et al [3] |
| 8.753  | 5.093  | CVD | C (B6C2) | Will et al [6] |
| 8.634  | 5.128  | CVD | N (B3N2) | Will et al [6] |
| 8.838  | 4.908  | calculation | none | Lee et al [7] |
| 8.81   | 5.01   | calculation | none | this work |
| 8.76   | 5.03   | calculation | C (B6C2) | this work |

For the growth of nano-sized crystals, it is more likely that the surface energy makes as large a contribution as the bulk energy. When we looked at the crystal structure of α-t boron, we noticed that its (100) surface has fewer bonds than the other surfaces. In fact, on the α-t nanowire obtained by Wang et al, the (100) surface appears very large, suggesting that it has much lower energy than the other surfaces. This prompted us to wonder whether the α-t crystal could be stabilized by its low surface energy, even though its cohesive energy is small, suggesting instability.

There have been few studies on the surface energy of boron. This is partly because the unit cells of boron crystals are large and the optimization of the geometry of the bulk and surfaces requires prolonged computation. We performed first-principle calculations of the surface energies of four polymorphs of boron and investigated whether a nano-sized α-t crystal could be stable [16, 17].

2. Computational Details

The calculation of the total energies and geometry optimization were performed using the CPMD code, version 3.9.1 [18, 19]. This code is based on the density functional theory with plane waves and pseudopotentials [20-22]. The norm-conserving Troullier-Martins-type pseudopotentials [23] were used. The generalized gradient approximation was included by means of the functional derived by Becke [24] and by Lee, Yang, and Parr [25]. An energy cutoff of 50 Ry for the plane-wave expansion was sufficient to provide a convergence for total energies and geometries. We have already confirmed in a previous study [26] that the total energies converged at a smaller cutoff of 40 Ry for this pseudopotential. Because the unit cell is large, the k-point sampling in the total energy calculation was performed using Monkhorst-Pack sampling [27] of a (2 × 2 × 2) mesh. The results were compared with those of a finer mesh, and it was found that the difference in the total energy per atom was less than 6 × 10⁻³ eV. In some cases, a larger unit cell was required to construct a model of a particular surface. For example, the (111) surface of a rhombohedral structure needs a hexagonal lattice that contains three times as many atoms as the primitive unit cell. For these larger cells, the calculations were performed only at the Γ point, and a good convergence was confirmed by comparison with a (2 × 2 × 2) mesh. Calculations were performed on a parallel computer (Hitachi SR11000) using a message-passing interface. Typically, 16 CPUs were used and the computational times for a geometry optimization were a few days to a few weeks.

To evaluate the surface energy, the total energy of the bulk was first calculated. A space of about 7 Å was then inserted at a certain cross section to generate a surface and the total energy was recalculated. The geometries were optimized in both calculations. The difference between the two total energies divided by the surface area was defined as the surface energy. The space of 7 Å was
sufficiently wide to render the interaction between surfaces negligible. We assumed that no structural defects like twining occur.

There are an infinite number of ways of inserting surfaces, and no strict proofs exist that a given set of surfaces is sufficient to reach the minimum surface energy. However, the experience of crystallography tells us that surfaces with high Miller indices rarely appear. In addition, surfaces that cut fewer bonds have inherently less surface energy, and those surfaces that make the crystal shape round also reduce the surface area. From these considerations, we lay down the following criteria for choosing surfaces: (i) surfaces with Miller indices of up to two; (ii) surfaces cutting fewer bonds; and (iii) surfaces that make the crystal shape round. The selected surfaces (cross sections) are indicated by red lines in figure 1.

Aside from the α-rh structure, fractional occupation sites exist for boron atoms. Because the unit cells for such structures are large, the fractional occupation does not have much effect on the surface energy. We assumed the number of atoms in a unit cell to be 105 for β-rh, 50 for α-t, and 196 for β-t.

3. Results and Discussion
First, we calculated the lattice constants of α-t boron and compared them with the experimental values listed in table 1. Our calculation indicates that pure α-t boron B₉‴ has a longer a and a shorter c value than a and c in B₉₋₆C. The calculation by Lee et al [7] also showed a similar trend. Among the experimental lattice constants listed in table 1, the results of Wang et al [12], who insist that their nanowire included no impurities, show a longer a and a shorter c than the other results. This means that their α-t nanowire is almost pure, or at least much purer than the others. Their experiment adopted LA without using any catalyst, giving little probability that impurities had contaminated their sample.

The calculated surface energies are exhibited in figure 2. The minimum-energy surfaces in the same Miller index group are excerpted from references [16, 17]. It is seen that α-t boron has the lowest average surface energy, as we had expected. Notably, the four main surfaces of (100), (001), (101),

![Figure 1. Atomic structures and surfaces of α-rh, β-rh, α-t and β-t boron.](image-url)
and (110) are the lowest of all the surfaces. \(\beta\)-t boron is the second lowest on average, followed by \(\beta\)-rh and \(\alpha\)-rh boron. The surface energies of \(\beta\)-rh and \(\alpha\)-rh have certain similarities, probably due to structural parallels. Both have a rhombohedral symmetry, and the orientations of the \(B_{12}\) icosahedra are the same, except that \(\beta\)-rh boron has additional \(B_{28}\) subunits at the center.

![Figure 2. Calculated surface energies of boron.](image)

![Figure 3. Equilibrium shapes of boron crystals calculated from Wulff’s theorem. The surfaces are labeled with Miller indices and equivalent surfaces in a crystal are the same color.](image)

When all the surface energies of a crystal are known, the crystal shape that minimizes the total surface energy at a constant volume is given by Wulff’s theorem [28, 29]. The theorem states that the distance from the crystal center to a surface is proportional to its surface energy per unit area. Low-energy surfaces are closer to the center and, as a result, exhibit a larger surface area. The crystal shapes of the four boron polymorphs obtained by Wulff’s theorem are shown in figure 3. The surfaces are labeled by their Miller indices. Equivalent surfaces are given the same color. It is interesting that the (100) surface appears very large in \(\alpha\)-t boron, as was observed in the experiment by Wang et al [12]. Its rectangular shape would appear to make it suitable for nanowire growth. \(\beta\)-t boron has a round shape which results from its isotropic surface energies. The structure of \(\beta\)-t boron is rather complicated, since it includes 196 atoms per unit cell, which means that the number of cut bonds does not differ very much between each surface. The shapes of \(\beta\)-rh and \(\alpha\)-rh boron are similar to each other as would be expected from their surface energies. \(\beta\)-rh boron has additional small faces because its \(B_{28}\) subunits make the surface energy more isotropic than that of \(\alpha\)-rh boron.

Once the crystal shape has been determined, it is easy to calculate the total surface energy. When the number of atoms is \(N\), the surface area and energy are proportional to \(N^{2/3}\); since the surface area is proportional to \(v^{2/3}\), where \(v\) is the crystal volume, and \(v\) is proportional to \(N\). The total energy of the crystal \(E_{\text{tot}}\) can be expressed as

\[
E_{\text{tot}} = -C_s N + C_s N^{2/3}.
\]  

The first term is the bulk part and \(C_s\) is equal to the cohesive energy per atom. The second term is the surface term. \(C_s\) can be calculated from the surface energy, crystal volume, and atom density. The
coefficients \( C_\alpha \) and \( C_\beta \) are listed in table 2. A comparison of \( C_\alpha \) values shows \( \alpha \)-rh boron to be the most stable and \( \alpha \)-t boron the most unstable. On the other hand, a comparison of \( C_\beta \) values shows \( \alpha \)-t boron to have an extremely low (stable) value, with \( \alpha \)-rh being the most unstable.

| \( C_\alpha \) (eV/atom) | \( C_\beta \) (eV/atom\(^2\)) | atom density (atoms/\(\text{Å}^3\)) |
|--------------------------|-------------------------------|---------------------------------|
| \( \alpha \)-rh           | 5.98                          | 2.48                            | 0.137                                     |
| \( \beta \)-rh             | 5.97                          | 2.16                            | 0.128                                     |
| \( \alpha \)-t             | 5.91                          | 1.78                            | 0.129                                     |
| \( \beta \)-t              | 5.96                          | 2.08                            | 0.130                                     |

Table 2. Calculated coefficients \( C_\alpha \), \( C_\beta \), and atom densities used for the calculations.

| \( \alpha \)-t | \( \beta \)-t | \( \beta \)-rh | \( \alpha \)-rh |
|----------------|---------------|----------------|----------------|
| \( N_c \)     | 216           | 254            | 1000           |
| \( \beta \)-t  | 512           | 8000           |                |
| \( \beta \)-rh | 32800         |                |                |
| \( \alpha \)-rh| 32800         |                |                |

Table 3. Critical sizes of boron crystals calculated with equation (2).

The total energy of the crystal is dominated by \( C_\alpha \) when \( N \) is large, and by \( C_\beta \) when \( N \) is small. When there are two phases of \( \alpha \) and \( \beta \) satisfying \( C_\alpha^{\alpha} > C_\beta^{\beta} \), \( C_\alpha^{\alpha} > C_\beta^{\beta} \), where the superscripts \( \alpha \) and \( \beta \) correspond to each phase, phase \( \alpha \) is more stable for large \( N \) and phase \( \beta \) for small \( N \). The critical size, \( N_c \), at which the total energies of the two phases become equal is calculated from equation (1) as

\[ N_c = \left\{ \frac{(C_\alpha^{\alpha} - C_\beta^{\beta})}{(C_\alpha^{\beta} - C_\beta^{\beta})} \right\}^{1/3}. \]  

(2)

The critical sizes for each boron polymorph are listed in table 3. For \( \alpha \)-t boron, the \( N_c \), against \( \beta \)-t (216) is lower than that against \( \beta \)-rh (254) and \( \alpha \)-rh (1000). As a result, \( \alpha \)-t boron is the most stable when \( N \) is between 0 – 216. In the same way, \( \beta \)-t, \( \beta \)-rh and \( \alpha \)-rh boron are the most stable between 216 – 512, 512 – 32800 and 32800 –, respectively. \( \beta \)-t boron has a rather narrow region, which would make it hard to synthesize. \( \beta \)-rh and \( \alpha \)-rh boron have a wide stable region, suggesting that they are easy to synthesize.

The thickness of nanowires obtained in the experiment by Wang et al [12] was several tens of nanometers. This is much greater than the critical size of the \( \alpha \)-t crystal, even if the estimated value includes some degree of error. Therefore, if the nanowire is pure \( \alpha \)-t boron, it must be in a metastable state. In an equilibrium state, according to Wulff’s theorem, the aspect ratio \( c/a \) of an \( \alpha \)-t crystal shape is equal to the ratio between the surface energies of the (001) and the (100) surfaces, and is estimated from the values in figure 2 to be 1.09. In real nanowires, the aspect ratio is much larger than this estimated value, which makes it likely that \( \alpha \)-t nanowires grow via a non-equilibrium process. Below we propose some possible growth mechanisms for \( \alpha \)-t nanowires.

The first possibility is that \( \alpha \)-t nanowires grow via a vapor-solid (VS) process. In this case, the growth rate is dominated by the sticking probability of vapor atoms to the surface rather than by the surface energy itself. The difference between the sticking probabilities of the (001) and the (100) surfaces could be greater than the difference between their surface energies, with the result that nanowires should grow more rapidly in the <001> direction than in the <100> direction. The second possibility is that \( \alpha \)-t nanowires grow via a vapor-liquid-solid (VLS) process. In this case, the nanowires would grow in the direction normal to the surface on which a liquid droplet preferably remains. The binding energy between the droplet and the surface determines which surface is preferred. It is difficult to calculate the binding energy because the droplet is in a liquid state. It is, however, logical to expect binding energy to be correlated to the surface energy, since the surface structures are identical. A surface with a higher surface energy would have a higher binding energy to the droplet, so that the droplet would prefer the (001) surface to the (100) surface.

In summary, the following processes are suggested as the growth mechanism of pure \( \alpha \)-t nanowires.
(i) First, an equilibrium nucleation takes place of an $\alpha$-t boron crystal that is smaller than $N_c = 216$.

(ii) Second, based on this nano-sized nucleus, the crystal, in a metastable state, grows more rapidly in the <001> direction than in the <100> direction. This may be due to the difference between sticking probabilities (VS process) or between the binding energies of the droplet on the surface (VLS process).

In the experiment by Wang et al [12], the dimensions of the nanowire were not actually tetragonal, i.e., $a_1 b_2$. The reason for this cannot be explained by our calculations, since the surface energies of the $a$ and $b$ surfaces in pure $\alpha$-t boron are identical. We speculate that the lack of tetragonal dimensions may be due to the presence of traces of impurities below the detectable level or to the experimental conditions, such as the angle of the laser beam.

The reason that pure $\alpha$-t is formed only in gas-phase syntheses, such as LA, is that in the gas phase, the fluctuations in the atom density are large, allowing small ($N < N_c$) clusters to exist as isolated entities. We speculate that LA, where a high temperature and a low density are achieved, is superior to CVD for the synthesis of $\alpha$-t boron crystals.

4. Conclusions

It has been proven that pure $\alpha$-t boron, despite its low cohesive energy, can exist as a nano-sized crystal because of its low surface energy. The calculated critical (maximum) number of atoms in the $\alpha$-t crystal is 216. Since the $\alpha$-t nanowire obtained in the experiment is much larger than this, it is probably in a metastable state. The difference in the surface energies explains why the nanowire grows in the $c$ direction. The calculated lattice constants of pure $\alpha$-t boron and $\alpha$-t $\text{B}_5\text{C}_2$ also agree with those determined experimentally by Wang et al [12], in which pure $\alpha$-t has a longer $a$ and a shorter $c$ than $\alpha$-t $\text{B}_5\text{C}_2$. We propose a growth mechanism for $\alpha$-t boron from the viewpoint of surface energies. Because boron clusters need to be isolated to form an equilibrium $\alpha$-t nucleus, laser ablation, in which the fluctuation of density is large, would favor the synthesis of $\alpha$-t boron.

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