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Role of hydrogen in the growth of boron nitride: Cubic phase versus hexagonal phase

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ABSTRACT

Hydrogen (H) behavior in crystal boron nitride (BN) has been systematically investigated by first-principles calculation. We find that H prefers to reside in the hexagonal phase (*h*BN) rather than the cubic phase (*c*BN). These kinds of H tend to gather to form clusters. In *h*BN, H can terminate a framework around an impurity-induced sp^3 nucleus, thereby suppressing the *c*BN growth. This explains why there is no significant improvement in the *h*BN-to-*c*BN transition after aluminium (Al) doping.

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1. Introduction

The binary semiconductor boron nitride (BN) has extraordinary properties and is regarded as an important candidate for electronic, optical, and other engineering applications [1–4]. There are two frequently used BN crystals: the hexagonal BN (*h*BN) and the cubic BN (*c*BN). The *h*BN phase with a direct band gap of 6 eV holds promise for ultraviolet device applications [4]. The *c*BN phase has a wide band gap and shows high thermal conductivity and extreme hardness, which makes it suitable for high-temperature electronic devices and use as an abrasive [5–7]. To synthesize pure BN crystal, especially the high-quality *c*BN, hydrogen (H) is a common background impurity during the CVD growth process [8–11]. As a result, a significant amount of H is unavoidably present in BN, and it impacts both material quality and device performance [12].

However, the behavior of H during the growth of BN is not well understood, especially at the microscopic scale. H prefers etching the sp^2-bonding phase to the sp^3-bonding phase. This etching selectivity is the key to synthesizing high-quality diamond [13]. However, it has been argued that H exhibits no significant etching selectivity for diamond-like *c*BN or graphite-like *h*BN [14]. So the growth of high-quality *c*BN is a more challenging task. In fact, intentional doping has also been used in an attempt to promote the growth of *c*BN. So the defect physics of H on BN as well as its doped sample is a worthy topic for further exploration.

Through first-principles calculation, we proved that H is more likely to be incorporated during the growth of *h*BN rather than that of *c*BN. During *h*BN growth we were surprised to discover that the formation energy of H can be reduced by increasing its concentration. At low concentrations, H generally prefers the H_2 molecular form. However, at high concentrations, a new form of H called H_2^{**} forms—in which one H binds to B and another binds to the neighboring N. By Al doping, Al_B serves as a cubic nucleus in *h*BN. However, the presence of H prevents additional B and N from binding to the nucleus and ultimately suppresses the growth of *c*BN.

2. Calculation details

Our first-principles calculation is based on density functional theory (DFT) within local density approximation (LDA) [15]. The projector augmented-wave potentials [16] are used as implemented in the VASP code [17]. The cutoff energy for the plane-wave basis is 400 eV. We obtained the lattice parameters a = 3.583 Å for *c*BN, and a = 2.492 Å, c/a = 2.604 for *h*BN. Both lattice constants a are only 1% smaller than experiment, and the c is

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smaller than experiment by 3% [18]. For defect calculations, large enough supercells are employed for *c*BN (216 atoms) and for *h*BN (200 atoms). Geometry optimization with $2 \times 2 \times 2$ Monkhorst–Pack *k*-point mesh is carried out until the Hellman–Feynman force on each atom is less than 0.05 eV/Å.

3. Results and disscusion

3.1. Structural form and stability

First, we studied H in *c*BN and *h*BN; their stability can be quantitatively reflected by formation energy. Following Ref. [19], the formation energy of a defect with *n*H atoms in *c*BN or *h*BN can be defined as:

$$E^f(n\mathrm{H}) = E_{tot}(n\mathrm{H}) - E_{tot}(bulk) - n\mu(\mathrm{H}), \tag{1}$$

where $E_{tot}(n\mathrm{H})$ is the total energy of a supercell containing *n*H atoms in BN. $E_{tot}(bulk)$ is the total energy of the same supercell without defect. $\mu(\mathrm{H})$ is the chemical potential of H. Here, the growth or annealing condition defines the chemical potential for B and N. Under thermal equilibrium, the chemical potential of the host atom must satisfy $\mu(\mathrm{B}) + \mu(\mathrm{N}) = \Delta H_f(\mathrm{BN})$, where $\mu(\mathrm{B})$ and $\mu(\mathrm{N})$ are the chemical potentials of B and N, respectively, and $\Delta H_f(\mathrm{BN})$ is the formation enthalpy of BN in the cubic or hexagonal phase. The upper limit of the chemical potential is limited by its stable form under standard conditions. Here, B solid and N_2 gas are set as the limit and reference for the B/N chemical potential. So, the range of chemical potential is written as:

$$(\text{B-poor condition})\Delta H_f(\mathrm{BN}) \leqslant \mu(\mathrm{B}) \leqslant 0(\text{B-rich condition}) \tag{2}$$

$$(\text{N-poor condition})\Delta H_f(\mathrm{BN}) \leqslant \mu(\mathrm{N}) \leqslant 0(\text{N-rich condition}) \tag{3}$$

Usually, the upper limit of the H chemical potential, $\mu(\mathrm{H})$, is defined by H_2 gas. Here, in the presence of N, we should also consider a secondary product (i.e., NH_3) during the growth. So, the chemical potential of H is defined as:

$$\mu(\mathrm{H}) \leqslant \frac{\Delta_f H(\mathrm{NH_3}) - \mu(\mathrm{N})}{3} \quad \text{and} \quad \mu(\mathrm{H}) \leqslant 0 \tag{4}$$

In Fig. 1(a), the formation energies of the H interstitial, H_2, and H complexes (labeled H_2^* and H_2^{**}) are shown. Generally, the energies in *h*BN are noticeably lower than those in *c*BN. We conclude that H prefers to reside in *h*BN. This is consistent with experiments involving low H concentrations in *c*BN [20]. The lowest-energy configuration in *c*BN is an H interstitial at the bond center, shown in Fig. 1(b). In this configuration, the inserted B–N bond is 52% longer than the normal one. So, the formation energy of this interstitial is quite high even under B-rich condition. We also studied H_2 molecules and H_2^* complexes according to the similar forms in silicon [21]. Like H_2 in silicon, H_2 favors the tetrahedral interstitial site (T_d) in *c*BN, see Fig. 1(b). But the bond length of H_2 is compressed from 0.76 Å (for free molecule) to 0.71 Å. Another interesting complex named H_2^* has one H at bond center and the other at the B antibonding site, see Fig. 1(b). But these two kinds of double H defects hold large formation energies (>7.22 eV for the H_2 and >6.47 eV for H_2^*). In other words, H is unlikely to be present in a substantial amount in *c*BN.

Compared to *c*BN, the formation energy of an H interstitial in *h*BN is much lower—i.e., 2.25 eV under B-rich condition. This is because no B–N bond is broken to produce an interstitial, see Fig. 1(c). Like H on graphene, an H interstitial in *h*BN tends to bond with B and then make the plane slightly bulged out (by ~0.1 Å). In *h*BN, the most stable form is an H_2 molecule (0.95 eV at B-rich condition), due to a large space for the insertion in Fig. 1(c). The H_2 stays at the center of a honeycomb parallel to the BN layer. Considering an unchanged bond length, this H_2 should hold the similar character as the free H_2 does. In terms of energy, another possible existing defect named H_2^{**} has one H connecting to B and the other connecting to neighboring N shown in Fig. 1(c). Clearly, these attached B and N atoms are in sp^3-bonding configuration. Therefore, it seems that H can aid the growth of *c*BN. However, an H atom prefers to have a single bond and finally limits the extension of the sp^3 framework.

Generally, various H-containing compounds are used as precursors in the CVD growth, so H is found in high concentration (>1%) in *h*BN [12]. However, the present formation energy (~1.0 eV for H_2 and ~1.6 eV for H_2^{**}) indicates it barely reaches such high concentration. For example, assuming a 500 °C growth temperature, the formation energy must be as low as 0.3 eV for a percent level incorporation in *h*BN. In fact, we note that infrared spectroscopy (IR) has observed vibration modes related to H–N and H–B bonds [22]. That raises an interesting question: can high-concentration H defects be more stable than the isolated one? We calculated the formation energy of H_2 and H_2^{**} with increasing concentration. The results are shown in Fig. 2. Here, the concentration is defined as the occupation percentage of available sites between two BN layers for H_2 and the coverage percentage on one BN plane for H_2^{**}. The averaged energy of H_2 decreases from ~1.0 eV at low concentration to 0.22 eV at 100% occupation. For H_2^{**}, the energy decreases from ~1.6 eV at low concentration to 0.20 eV at 100% occupation. As seen in Fig. 2 inset, the full covered BN plane by H_2^{**} is changed to a *zigzag*-like structure and results in lowering total energy. These results very clearly suggest that H_2 or H_2^{**} can automatically gather to form clusters in *h*BN. This low energy is consistent with a substantial amount of H in *h*BN in experiments [12,22].

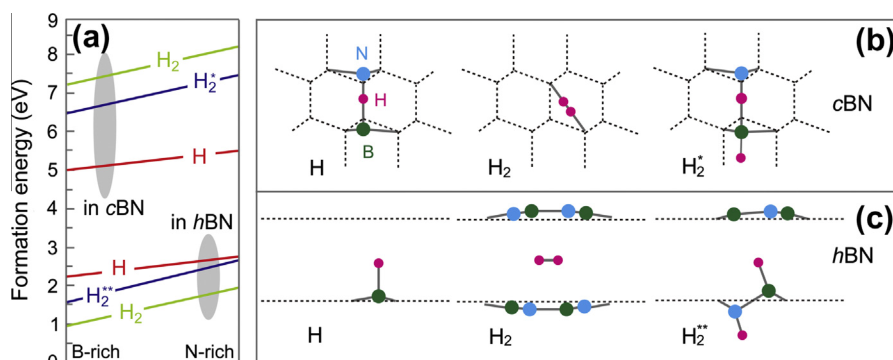

Fig. 1. (a) Formation energies of H defects as function of growth condition. (b) Schematic drawings of various H defects in *c*BN. (c) Same as (b) but for *h*BN. The perfect lattice grid is represented by dashed lines, while the H atoms as well as the B and N atoms that undergo significant relaxations are represented by spheres, as labeled in *c*BN.

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