Subsurface Nitrogen in Diamond (001)-2×1-H Studied by Density Functional Theory

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To populate nitrogen centers in the near-surface region of diamond, there has been recent effort [1-3] of using activated dinitrogen to impact fully hydrogenated diamond surfaces as synthesized by chemical vapor deposition. There is implication [2-3] of nitrogen into the subsurface region (depth: 6 ± 5 Å) of the same diamond (001)-2x1-H by low energy N_2^+ ions. It remains, however, unclear about the atomistic understanding into the configuration and bonding of the nitrogen species in the subsurface region of diamond (001)-2×1-H. Here, we present studies into subsurface nitrogen in diamond (001)-2x1-H by density functional theory simulations, revealing in each case information regarding structure, energy and vibration that depend on the atomistic coordination as detailed below.

1. Interstitial N_i Species. We have studied 10 configurations of a single interstitial nitrogen in the topmost 3 layers of diamond (001)-2x1-H. In all configurations, the carbon network is strongly distorted by an interstitial nitrogen atom, in which 2 carbon-carbon bonds are cleaved. The interstitial nitrogen is bound to 3 neighboring carbon atoms, of which one carbon becomes sp^2 hybridized. The stability of the interstitial configuration depends on the location of nitrogen and the direction of the formed C(sp^2)-N bond, exhibiting formation energies of +4.83 to +11.04 eV. The most characteristic mode of vibration arises from the C(sp^2)-N bond, i. e., stretch (1530 to 1901 cm^{-1}/ 189.7 to 235.8 meV) and swing (1101 to 1389 cm^{-1}/ 136.6 to 172.2 meV). Migration of nitrogen interstitial is also evaluated, involving a series of steps and intermediates; the rate determining step is of a barrier of 6.02 eV.

2. Substitutional N_s Species. We have also evaluated 3 configurations of a single substitutional nitrogen in the topmost 3 layers of diamond (001)-2x1-H. In all configurations, the carbon network is largely preserved, giving formation energy of +2.79 to +3.41 eV. The substitutional nitrogen is bound to four neighboring carbons, and the formed C-N bond is larger than a typical C-N single bond, giving the characteristic C-N swing vibration of 844 to 979 cm^{-1} (105 to 121 meV).

3. Dinitrogen N_{2i} Species. We have finally evaluated 6 configurations of a pair of nitrogen atoms in the topmost 3 layers of diamond (001)-2x1-H. Our computations were restricted to the N_{2i} species that mimics the encounter of an interstitial N_i and a substitutional N_s species. The formation energy depends on the location of N_{2i} and the direction of the formed N_i-N_s bond, ranging from +4.12 to +9.71 eV. The most characteristic motions of vibration arise from N-N stretch mode of 1419 cm^{-1} (176.0 meV), C-N swing mode of 968 cm^{-1} (120 meV) and N-N swing mode of 471 cm^{-1} (58.5 meV).

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