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ABSTRACT

We report the observation of substitutional silicon atoms in single-layer hexagonal boron nitride (h-BN) using aberration corrected scanning transmission electron microscopy. The images reveal silicon atoms exclusively filling boron vacancies. Density functional theory is used to study the energetics, structure, and properties of the experimentally observed structure. The formation energies reveal Si_B^{+1} as the most stable configuration. In this case, the silicon atom elevates by 0.66 Å out of the lattice with unoccupied defect levels in the electronic bandgap above the Fermi level. Our results unequivocally show that heteroatoms can be incorporated into the h-BN lattice opening the way for applications ranging from single-atom catalysis to atomically precise magnetic structures.

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The study of two-dimensional (2D) materials has, since the introduction of graphene,¹ become an active research field in materials science. Graphene was quickly followed by other 2D materials such as hexagonal boron nitride (h-BN)² and transition metal dichalcogenides³ which in contrast to graphene exhibit an electronic bandgap. h-BN has attracted attention due to its high thermal and chemical stability, high thermal conductivity, and low dielectric constant, besides its wide electronic bandgap,⁴ although due to its honeycomblike arrangement of *sp*²-hybridized structure that is almost a perfect match to graphene, it is most often regarded just as suitable substrate for graphene-based applications.⁵

Defects play a crucial role in semiconductors in determining the applicability of the material. For example, vacancies and impurities change the electronic and optoelectronic properties by adding localized defect levels into their bandgaps^{6–8} providing charge carrier traps and/or combination centers.⁹ Although silicon is the most often encountered impurity atom in graphene samples,^{10–12} it has not been until now observed in h-BN. In contrast, both oxygen and carbon have been found in single-layer h-BN, probably due to electron beam damage, during a scanning transmission electron microscopy (STEM) experiment.¹³ On the one hand, Si impurities in h-BN could be interesting from the material engineering point of view, especially for applications in electronics,^{14–17} quantum computing.¹⁸ and spintronic devices.^{19–21} On the other hand, they could be detrimental when h-BN is used as a gate dielectric in field-effect transistors. Previous theoretical studies have shown that silicon substitution in boron vacancies is more stable than substitution in

nitrogen vacancies.^{22–24} Both +1 and -1 states have also been considered in addition to the neutral state.²⁴ However, the number of valence electrons and the position of the defect levels have been ignored.

In this letter, we show atomic resolution STEM images of substitutional silicon impurities in h-BN with density functional theory (DFT) calculations and image simulations revealing the details of the atomic configuration. The formation energies for each of the possible silicon substitutions (in boron, nitrogen, and double vacancies) are calculated with different charge states. In accordance with the experiments that show exclusively impurity atoms in the B lattice site, our simulations reveal $\mathrm{Si}_{\mathrm{B}}^{+1}$ as the configuration with the lowest formation energy. Our results demonstrate the possibility of incorporating heteroatoms into h-BN opening the way for atomic-scale engineering of the material for applications.

Single-layer h-BN suffers from significant electron beam damage in transmission electron microscopy experiments,^{14,25,26} caused by a combination of knock-on processes and ionization damage. The vacancies created during electron irradiation not only tend to grow fast into triangular holes but can also be filled by atoms from the ubiquitous hydrocarbon-based contamination covering most samples, as presumably happened in the study presented in Ref. 13. In contrast to such nonintrinsic defects created during the experiment, we discuss here intrinsic impurity atoms that were found in the samples after preparation with no additional processing and only a minimal electron dose.

We point out that unlike most h-BN samples that are prepared via mechanical exfoliation, ours were grown via chemical vapor

deposition (Graphene Laboratories, Inc.), which may explain why Si impurities in h-BN have not been reported until now. The samples were directly transferred onto golden transmission electron microscopy grids with a perforated amorphous carbon membrane (Quantifoil[®]) without a polymer. Copper was etched in FeCl overnight, and the samples were baked in vacuum at 150 °C overnight before being inserted into the microscope. Figure 1(a) shows an atomically resolved medium angle annular dark field (MAADF) image of the suspended h-BN membrane with four silicon impurity atoms in the h-BN lattice. All images were acquired with a Nion UltraSTEM 100 microscope²⁷ in Vienna at 60 kV with near-ultrahigh vacuum at the objective area (pressure $<10^{-9}$ mbar).²⁸ The beam convergence semiangle was 30 mrad, and the MAADF detector angular range was 60–200 mrad. The typical beam current of the device is on the order of 30 pA.

Silicon can be easily distinguished by its higher contrast as compared to boron and nitrogen atoms.¹³ In all images, Si impurities are on boron sites [see Fig. 1(b)]. The image intensities are shown in Fig. 1(c) along the path marked by arrows in Fig. 1(b), normalized to the intensity corresponding to a single boron atom. The intensity ratio between Si and B is expected to be $(14/5)^{1.64} = 5.41$,¹³ close to our experimental value of 5.25. Although the substituted silicon atom is stable enough to allow its repeated scanning, it cannot sustain the electron dose required for electron energy loss spectroscopy¹¹ or energydispersive X-ray spectroscopy to independently confirm the chemical identity of the individual impurity atoms. Since the hydrocarbonbased contamination covering much of the sample also contains silicon, spectra recorded over larger areas would remain inconclusive. Figure 1(d) shows a MAADF image simulated with the QSTEM package (https://www.physics.hu-berlin.de/en/sem/software/software_ (stem)²⁹ of the relaxed structure (+1 charge state) with good agreement between the projected Si-N distances between the nearest nitrogen atoms and the impurity in calibrated experimental and simulated images. For both cases, the projected Si-N distance is around 1.55 Å. The distance between neighboring nitrogen atoms shows an increase from 2.51 Å in pristine h-BN to 2.74 Å around the impurity, consistent with the optimized model structure.

The typical hydrocarbon-based contamination that covers nearly all graphene and h-BN samples contains a large number of silicon atoms. In fact, it is possible to dope such samples with Si simply by



FIG. 1. Silicon substitution at the boron vacancy in h-BN. (a) Experimental MAADF image of multiple Si atoms in h-BN (bright points) recorded with a relatively low dose to avoid electron-beam damage. (b) A close-up MAADF image of Si_B (the brightest atom). N and B atoms can be distinguished based on their contrast (brighter and darker, respectively). (c) Line profile showing the intensities between the arrows in panel (b). (d) Simulated MAADF image of Si_B⁽⁺¹⁾. The scale bars are 0.5 nm.

creating vacancies into them at elevated temperatures.³⁰ Hence, it is natural to assume that this is the source of Si atoms found in our h-BN samples.

We turn to density functional theory (DFT) calculations [as implemented in the Vienna *ab initio* simulation package (VASP)³¹] to try to understand why they are exclusively found in the B lattice sites. The electron exchange and correlation was treated by the Perdew-Burke-Ernzerhof (PBE) functional.³² The total energy of the system was calculated via the pseudopotential-momentum-space formalism using the projector-augmented-wave (PAW) method.³³ The Kohn-Sham wavefunctions are expanded over plane wave basis sets with the kinetic energy cut off set to 525 eV. Converged locally optimized configurations and formation energies were found for a supercell of $8 \times 8 \times 1$. The interlayer vacuum space of 43.46 Å was selected according to "special vacuum" proposed in Refs. 34 and 35. The Brillouin-Zone integration was done over a Γ -centered 5 \times 5 \times 1 k-point mesh. The damped molecular dynamics method was used to optimize the ionic degrees of freedom until residual forces were below 0.01 eV/Å. We point out that although it is known that the bandgaps calculated using PBE underestimate the true bandgap of semiconductors, it yields formation energies similar to those calculated with the HSE (Heyd-Scuseria-Ernzerhof)³⁶ formalism.³⁷ This allows rescaling of the electron chemical potential of PBE calculations using the difference in the bandgap obtained from the two methods, leading to a significant saving in the computational cost. Here, HSE (HSE06 functional with 0.25 fraction of exchange³⁸) was used to calculate the bandgap of bulk h-BN (5.72 eV as compared to 4.48 eV calculated with PBE) for this purpose.

For each possible impurity site in h-BN, we first structurally optimize the structure and then calculate its electronic properties and formation energy. The calculations are repeated for different charge states. Figures 2(a) and 2(b) show the top and side views of the structures for the neutral state of Si_B. The N-Si bond length is found to be \sim 1.72 Å, which is significantly longer than \sim 1.45 Å between B and N in the pristine structure and 1.55 Å measured from the experimental images. The silicon atom rises 1.241 Å above the h-BN plane. The side view of the structures corresponding to different charge states is shown in Figs. 2(c) and 2(d). As for the +1 charge state, the N-Si bond length drops to 1.63 Å. For the -1 charge state, the bond length becomes 1.82 Å. Simply taking into account the projected distance between silicon and neighboring nitrogen atoms is not conclusive enough to estimate the charge state of the defect. The simulated MAADF images show the projected Si-N distance within 1.53-1.55 Å, which are very close to the calibrated distances of experimental data. Negative charge elevates Si further away from the negatively charged N neighbors, whereas positive charge has the opposite effect.

The band structures of silicon substitution in boron vacancies at different charge states are plotted in Figs. 2(e)-2(g). The Fermi level is set to zero. The red (blue) lines correspond to the spin up (down) band structure. For the neutral state, Si substitution adds two defect states within the bandgap, where only one of the defect levels (spin down) is empty. Therefore, Si_B has only two expected charge states (-1 and +1); adding further electrons or holes to the structure leads to electrons in the nearly free-electron (NFE) state of the conduction band minimum (CBM) or holes at the valence band maximum (VBM).^{37,39} This NFE state is 2 Å away from the h-BN plane.⁴⁰ In the



FIG. 2. Atomic and band structure of Si in the boron vacancy. (a) Top view of locally optimized Si_B with the Si-N bond length shown. Side view of (b) Si_B¹, (c) Si_B⁻¹, and (d) Si_B⁺¹ including the estimated elevation of silicon with respect to the h-BN plane. The PBE-calculated spin-polarized band structure of (e) Si_B⁻¹ with two defect levels in the bandgap and spin-unpolarized band structures of (f) Si_B⁻¹ and (g) Si_B⁺¹.

+1 and -1 charge states, the system becomes spin-unpolarized. An interesting case is the band structure of $\text{Si}_{\text{B}}^{-1}$ [Fig. 2(f)]. Here, the defect level is so close to the Fermi level that the added electron is almost free and thus easy to extract.

We calculate the defect formation energy using the supercell method⁴¹ for a charge state q as

$$f[X^{q}] = E_{tot}[X^{q}] - E_{tot}[host] - \sum n^{i} \mu_{i} + q[E_{F} + E_{VBM}] + E_{cor}$$

E

where $E_{tot}[X^q]$ is the total energy of the supercell containing a defect or impurity X and $E_{tot}[host]$ is the total energy for the equivalent supercell of a perfect crystal. n_i are the number of atoms which are added ($n_i > 0$) or removed ($n_i < 0$) from the supercell and μ_i are the chemical potentials of the constituent atoms *i*. The formation energy is expressed as a function of electron chemical potential (i.e., Fermi energy E_F with respect to the valence band maximum of the pristine structure). E_{corr} corresponds to all spurious electrostatic corrections due to employing the supercell method. We calculate the chemical potential for boron and nitrogen atoms as the total energy of β -rhombohedral boron (per atom), containing 106 atoms per unit cell,⁴² and half of the chemical potential of the nitrogen molecule (N₂). The chemical potential of silicon has been calculated from the total energy of bulk silicon (per atom).

The calculated Si_B formation energies in N-rich conditions are shown in Fig. 3. The formation energy for the neutral defect is around 0.46 eV, which is higher than the previously reported value of -0.29 eV, possibly due to the small vacuum size (15 Å) used in the earlier calculations.^{23,24} However, the most stable charge state for Si_B substitution is +1 which undergoes a slightly exothermic process. The



FIG. 3. Formation energy of Si_B. Formation energy as a function of the Fermi energy for different charge states in the N-rich environment.

defect energy transition states for e(+1/0) and e(0/-1) are expected to be at 0.61 eV and 2.96 eV with respect to VBM as calculated with the Perdew-Burke-Ernzerhof (PBE)³² functional. Taking into account the difference in the bandgaps calculated with PBE and HSE, as described above, we would expect the actual transition levels to be 1.23 eV and 3.58 eV above VBM. Both defect levels are considered deep and expected to influence the optical properties of h-BN.

For the h-BN layer which is on top of Cu(111), we expect that the copper (as during growth) Fermi level lies around 1.4–1.5 eV above the VBM of h-BN,^{43,44} and therefore, the Si_B should be in the neutral state. However, it has been shown that under an electron beam, BN-nanotubes are positively charged, which is attributed to emission of secondary electrons that shift the Fermi level to VBM, and Si_B switches to the +1 state.⁴⁵

Figures 4(a) and 4(b) show the locally optimized structure of silicon substitution in the nitrogen site in h-BN in its neutral state. Compared to Si_B, in Si_N, the silicon atom extrudes higher out from h-BN. The distance between silicon and the h-BN plane is \sim 2.0 Å, and the bond length between silicon and neighboring boron atoms is



FIG. 4. Structure and formation energy of Si_N. (a) Top view of locally optimized Si_N^ substitution with the Si-B bond length and (b) elevation of the silicon atom. (c) and (d) Side views of the charged structures. (e) Formation energy for Si_N in a boron rich environment.

1.956 Å. This buckling could be attributed to the electrostatic repulsion between silicon and neighboring boron atoms. Bader analysis¹⁹ of charge density shows that the silicon atom has lost all valence electrons, while the neighboring boron atoms have lost a fraction of their electrons to the neighboring nitrogen atoms. Adding an electron (Fig. 4) would again slightly elevate the silicon atom. However, most of the charge is again transferred to the nitrogen atoms.

The formation energy for Si_N in the boron rich environment is shown in Fig. 4(e). E^f for the neutral defect is around 4.86 eV, which is high compared to silicon in the boron vacancy. Based on the band structure calculation (supplementary material), possible charge states range from -1 to +2. The most stable case is when the silicon atom is in neutral state. The transition level e(0/-1) is at 1.90 eV as calculated with PBE. By rescaling the Fermi energy based on the calculated HSE bandgap, we expected that this transition energy would rise to 2.51 eV.

We also calculated formation energy for silicon substitution in a double vacancy, where adjacent boron and nitrogen atoms are missing. The optimized structures are shown in Fig. 5. In this case, the h-BN monolayer remains almost flat with the silicon-boron bond length of \sim 2.09 Å and silicon-nitrogen bond length of \sim 1.78 Å. One added electron changes the bond length for Si-B and Si-N to \sim 1.96 Å and \sim 1.88 Å, respectively. From the band structure calculation (supplementary material), it is evident that both +1 and +2 states are possible. However, silicon is pushed even more toward the nitrogen atoms due to electrostatic repulsion between boron atoms and the impurity. The bond lengths in this case are \sim 2.20 Å and \sim 1.73 Å for Si-B and Si-N bonds, respectively. E^{f} values are shown in Fig. 5(e). Interestingly, for the neutral structure of Si_{BN} , it is around 5.25 eV, which is slightly higher than Si_N substitution despite the flat structure. The +2 charge state has the highest formation energy, and the PBE calculated transition levels are 0.51 eV for (+1/0) and 3.11 eV with respect to VBM. For the HSE method of calculation, we would expect transition levels for e(+1/0) and e(0/-1) to be 1.12 eV from VBM and 2.00 eV from CBM.

We further calculated the migration barrier for Si_B to pass from one side of the h-BN plane to the other, a process that has been recently observed in graphene.⁴⁶ The barrier was calculated with the



FIG. 5. Structure and formation energy of Si_{BN}. Optimized model for silicon in (a) neutral (Si_{BN}^0) , (b) negatively charged (Si_{BN}^{-1}) , and (c) positively charged (Si_{BN}^{+1}) states in a double vacancy. (e) Formation energy of silicon in a double vacancy.

nudged elastic band method.⁴⁷ The estimated energy barrier of 2.42 eV is much higher than 1.08 eV for silicon substitution in graphene,⁴⁸ which could be attributed to the ionic bonding between silicon and h-BN. The same transition can be achieved by providing the Si atom 3.28 eV of kinetic energy, as confirmed using the molecular dynamics calculation with DFT (0.5 fs time step). This amount of energy can be transferred to a static Si atom by an electron with a kinetic energy of 40.5 keV and easily achieved under our experimental conditions (acceleration voltage: 60 kV). Thus, most Si atoms are expected to face away from the electron beam.

In this work, we present the direct experimental observation of Si impurities in a free standing monolayer of hexagonal boron nitride (h-BN) using scanning transmission electron microscopy. Our density functional theory calculations show that Si atoms have the lowest formation energy in a boron vacancy, which is also the only experimentally observed configuration. Our simulations indicate +1 as the most likely charge state. Although the origin of Si atoms in our samples remains unknown, the results expand the number of observed impurity atoms in h-BN from the previously reported C and O to an element from the third row of the periodic table. This shows that heteroatom doping of h-BN with heavier elements is possible similar to graphene,^{49,50} opening the way toward applications ranging from single-atom catalysis to atomically small magnetic structures.

See the supplementary material for the details about experimental and theoretical methods, band structure of Si_N and Si_{BN} in their possible charge state, and the formation energies of Si_B and Si_N under other growth conditions. References 27, 28, 30, 32–39, and 48 are also cited.

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