

Silicon Substitution in Monolayer Hexagonal Boron Nitride

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Defects play a crucial role in semiconductors in determining the applicability of the material. Vacancies and impurities change the electronic and optoelectronic properties of semiconductors by adding localized defect levels into their band gaps [1]. Since two-dimensional materials, such as graphene and h-BN consist of just one atomic layer, their properties are especially easily changed by incorporation of defects and impurities. Silicon atoms are well-known ubiquitous impurity in graphene samples, whereas no intrinsic impurities have been reported until now for h-BN [2].

In this work we represent the atomic resolution scanning transmission electron microscopy (STEM) images of substitutional intrinsic Si impurities on a free standing monolayer of h-BN. Multi-layered hBN has attracted much of attention over the past two decades due to its chemical stability, negative electron affinity and, most importantly, its finite band gap with potential to be incorporated into existing silicon based electronic devices as a dielectric material. Computational studies suggested that vacancies and also heteroatoms in h-BN could be beneficial for applications in electronics, quantum computing and spintronic devices.

Fig. 1a shows an atomically resolved medium angle annular dark field (MAADF) image of the suspended h-BN membrane with four silicon impurities filling vacancies in h-BN lattice. Interestingly, all observed silicon substitutions were on boron sites. A close-up MAADF image of one of the silicon impurities is shown in Fig 1b. The intensity of the constituents in ADF images is proportional to the atomic number by, which allows a straightforward identification of the impurity atoms [3]. The ADF intensities directly reveal the possible atomic number of the impurity through a comparison with boron and nitrogen (Fig. 1c). The simulated STEM image of the relaxed structure of Si in boron site is shown in Fig 1d.

In order to understand the exclusive substitution of Si in boron site of h-BN, we used density functional theory (DFT) and calculated the optimized structures and formation energies of all possible impurity sites. The existence of silicon in h-BN distorts the planar structure. The formation energy for the defects along with their different charge states are calculated. Fig 2a shows the optimized structure of Si at boron site (in neutral charge state) with indication of buckling height. Figure 2b shows the formation energies and defect energy transition states.

The results are compared to those of silicon in the nitrogen site or in a double vacancy created by the removal of neighbouring boron and nitrogen atoms. Figure 3a and 3b show the formation energies for the two last substitutions, respectively. Clearly, the silicon atom is more stable in boron site with slightly exothermic reaction compared to endothermic process at nitrogen and double vacancy substitutions.

We also attempt to calculate the migration barrier for silicon impurity in boron substitution from one side of the h-BN plane to another. The energy barrier estimation is based on the nudged elastic band

(NEB) method [4]. The energy barrier (Fig 4) is as high as 2.34 eV much higher than Silicon in graphene [5].

References:

- [1] J. Kotakoski, et al., Phys. Rev. Lett. 106, 105505 (2011).
 [2] Q. M. Ramasse, et al, Nano Lett. 13, 4989 (2013).
 [3] O. L. Krivanek, et al, Nature 464, 571 (2010).
 [4] G. Henkelman and H. Jónsson, J. Chem. Phys. 113, 9978 (2000)
 [5] T. Susi, et al., Phys. Rev. Lett. 113, 115501 (2014).
 [6] The authors acknowledge funding from FWF project no. P31605-N36

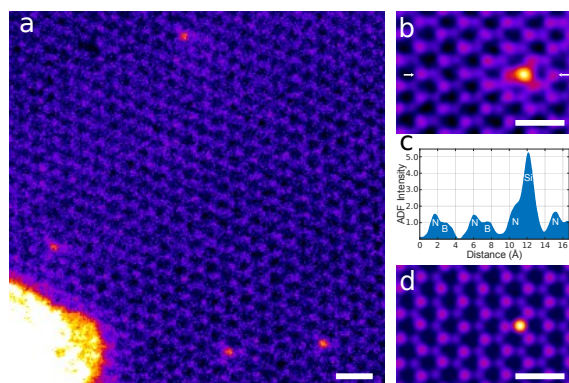


Figure 1. Si@B in h-BN. (a) Experimental MAADF image of multiple Si atoms in h-BN. (b) A close-up MAADF image of Si@B (c) Line profile showing the intensities between the arrows in panel b. (d) Simulated MAADF image. The scale bars are 0.5 nm.

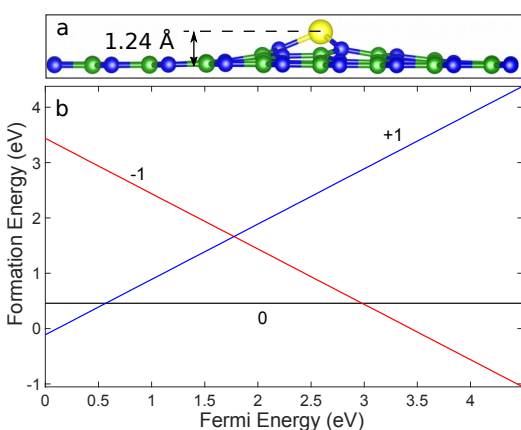


Figure 2. (a) Si@B side view. (b) Formation energy of Si@B site in N-rich condition.

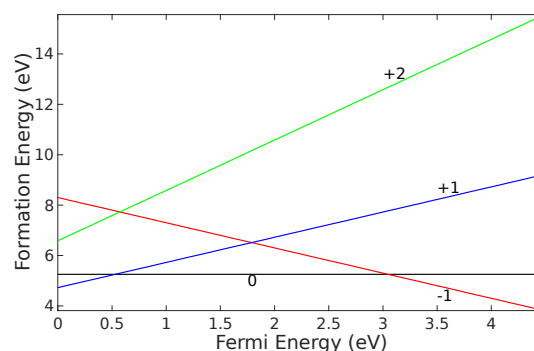
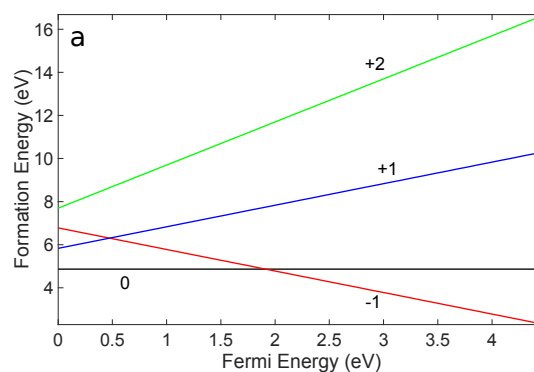


Figure 3. (a) Formation energy of Si@N in B-rich condition and (b) Si@BN site.

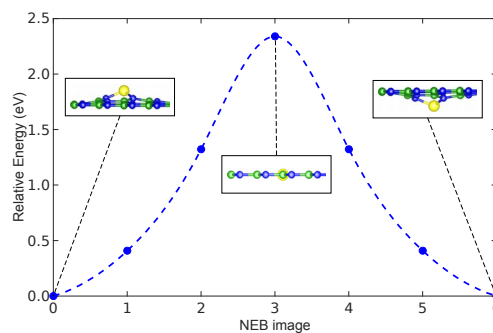


Figure 4. Migration energy barrier of Si in boron site through the h-BN layer.