Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Figures

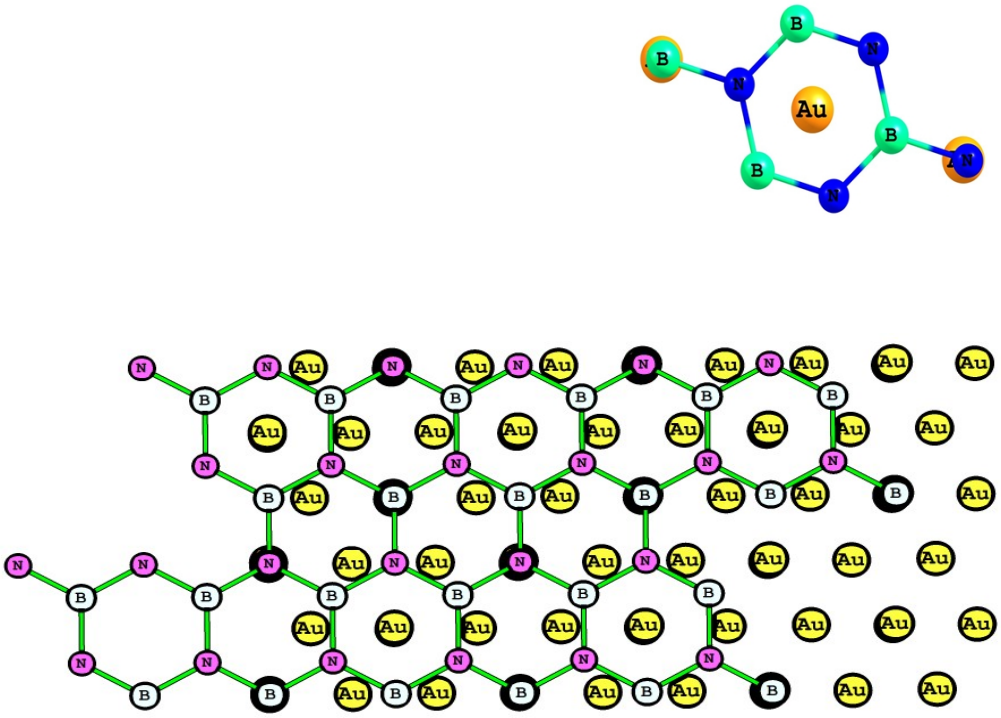

Figure S1: (Color online) A schematic illustration of the monolayer lattice commensurate with the Au (111) surface.

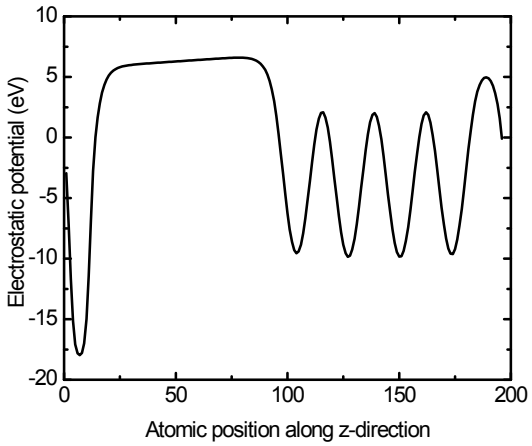

Figure S2: The planar average electrostatic potential along the z-direction for one unit cell of the silicon doped boron nitride monolayer with that of Au (111) surface.

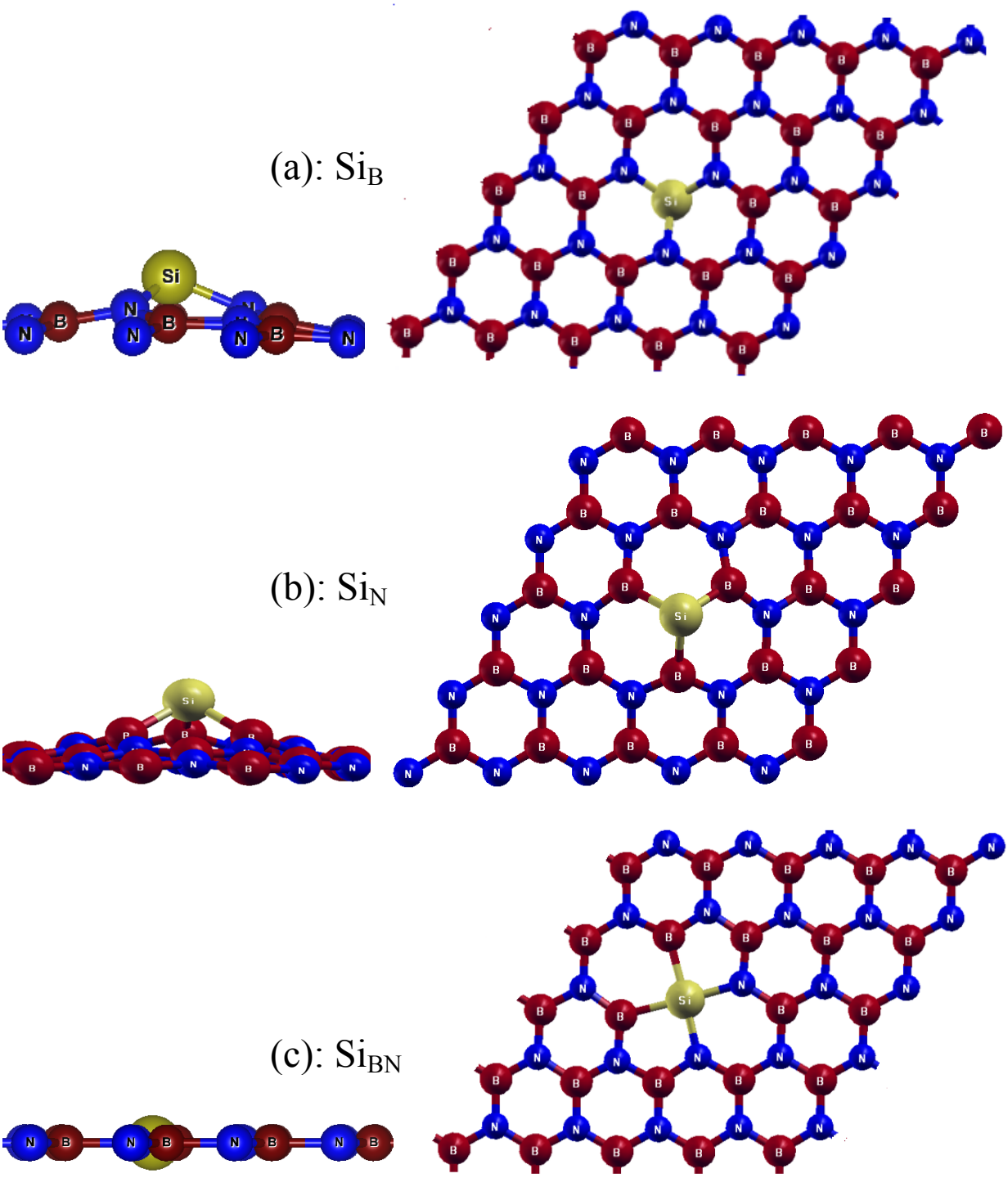

Figure S3: (color online). Side (left) and Top (right) views of Si doped BN monolayers: (a) 3-fold coordinated Si at B (Si_B), (b) 3-fold coordinated Si at N (Si_N), and (c) 4-fold coordinated Si at BN (Si_{BN}).

Formation Energy:

In order to investigate the stability of the dopant in the lattice, we define the formation energy E_f to represent the case of n_{Si} silicon atoms substituting n_B boron and n_N nitrogen atoms (note $n_B + n_N = n_{Si}$ for single-site doping only). E_f can then be calculated as

$$E_f = E_{tot}^{defect} - E_{tot}^{pristine} + n_B\mu_B + n_N\mu_N - n_{Si}\mu_{Si} \qquad (1)$$

where E_{tot}^{defect} and $E_{tot}^{pristine}$ are the calculated total energies of defective and pristine BN systems, respectively. μ_B, μ_N, and μ_{Si} are the chemical potentials of the elements present in the system. At equilibrium,

$$\mu_B + \mu_N = \mu_{BN} \qquad (2)$$

where μ_{BN} is the chemical potential per BN pair in a pristine h-BN monolayer. μ_{Si} is chosen to be the cohesive energy per atom of the Si bulk (= -4.63 eV [1]).

The choice of μ_B and μ_N is given by the growth conditions to be considered during the doping process. In the N-rich environment, μ_N is set to half of the binding energy of a N_2 molecule (E_b=-9.9 eV [26]). In the B-rich environment, μ_B is set to the cohesive energy of the α-boron bulk material (E_{coh}=-5.81 eV [2]).

The calculated formation energies are plotted as a function of μ_B in Fig. S3. The canted lines indicate the change of formation energies as μ_B increases to that of a B-rich environment. The horizontal lines are formation energies for a single Si dopant under the N-rich conditions. The crossing point of these lines represents the equilibrium condition in N-rich environment as shown in Fig. S3. The formation energy of the 4-fold Si_{BN} does not vary with μ_B due to the imposed constraint of the equilibrium condition (Eqn. 2). Thus, the formation of Si_B is always preferred over Si_N and Si_{BN} in the BN monolayer under either N-rich or B-rich conditions. A

comparison of our results with the results on the C-doped BN monolayer [12] shows a similar variation in the formation energy of C_B and C_N.

Note that the positive formation energy indicates that the substitutional doping requires energy to be available, since the doping process occurs under thermodynamical equilibrium with the atomic reservoirs. The calculated changes in the formation energies suggest that the Si substitution at the B/N site in the BN monolayer will be an energetically demanding process.

References:

1: N. Moll, M. Bockstedte, M. Fuchs, E. Pehlke, M. Scheffler, Application of generalized gradient approximations - the diamond-beta-tin phase-transition in Si and Ge, Phys. Rev. B, 1995, **52**, 2550.

2. K. C. Lau, R. Orlando and R. Pandey, First-principles study of crystalline bundles of single-walled boron nanotubes with small diameter, J. Phys.: Condens. Matter., 2008, **20**, 125202.

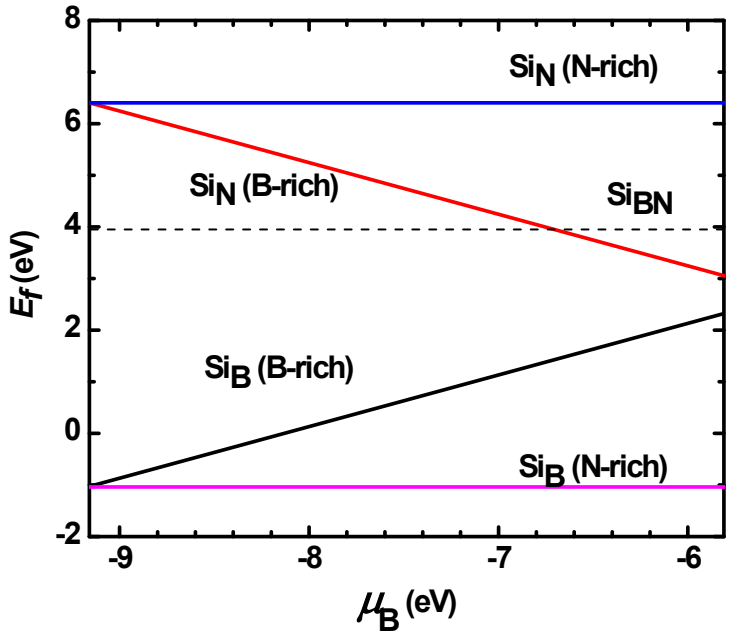

Figure S4: (color online) The calculated formation energies of Si_B, Si_N and Si_{BN} in the h-BN monolayer under N-rich and B-rich environments.

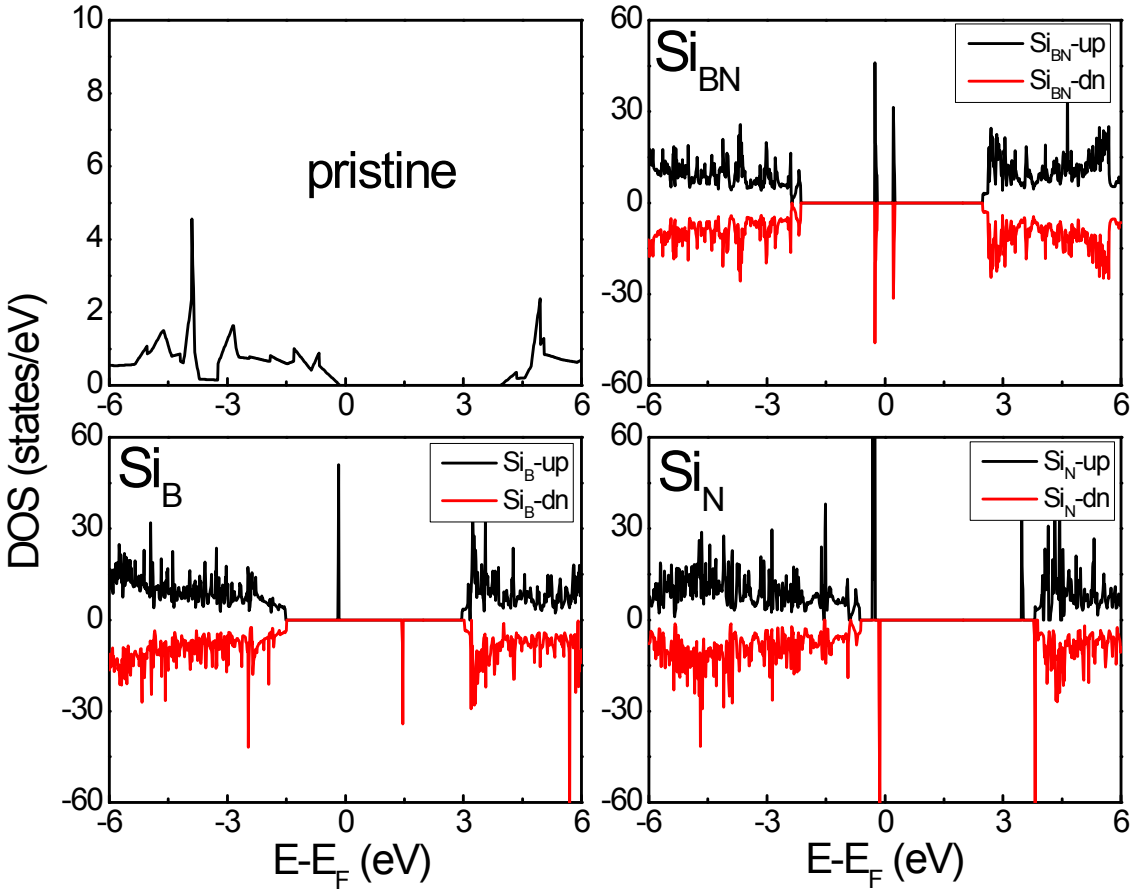

Figure S5: (color online) Total density of states of Si doped monolayers: (a) Si_B, (b) Si_N and (c) Si_{BN}. 'up' and 'dn' refer to the spin-up and spin-down components, and zero is aligned to Fermi energy (E_F) of the system.

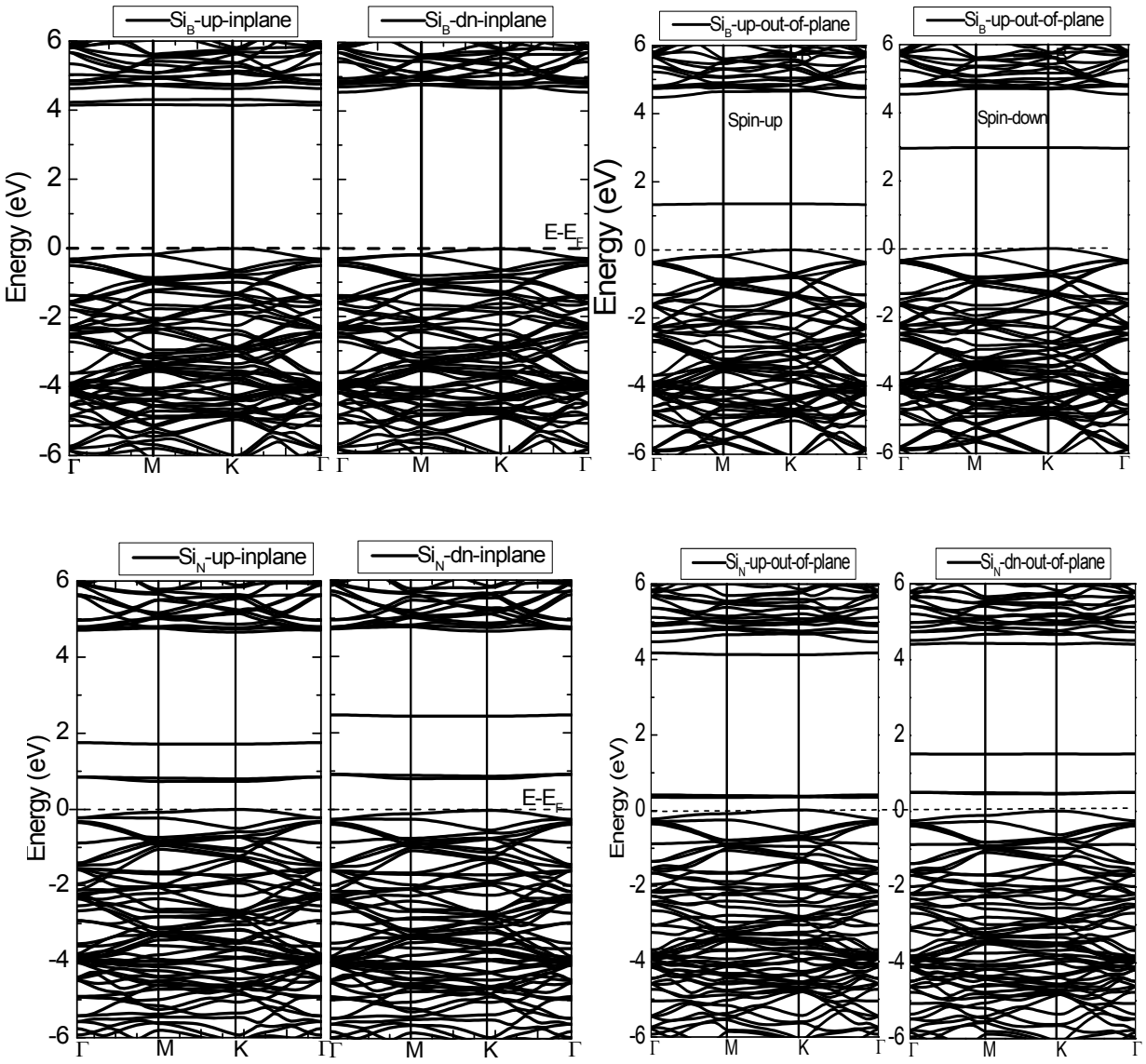

Figure S6: Band structure plots for in-plane and out of plane configurations of Si_B, and Si_N.

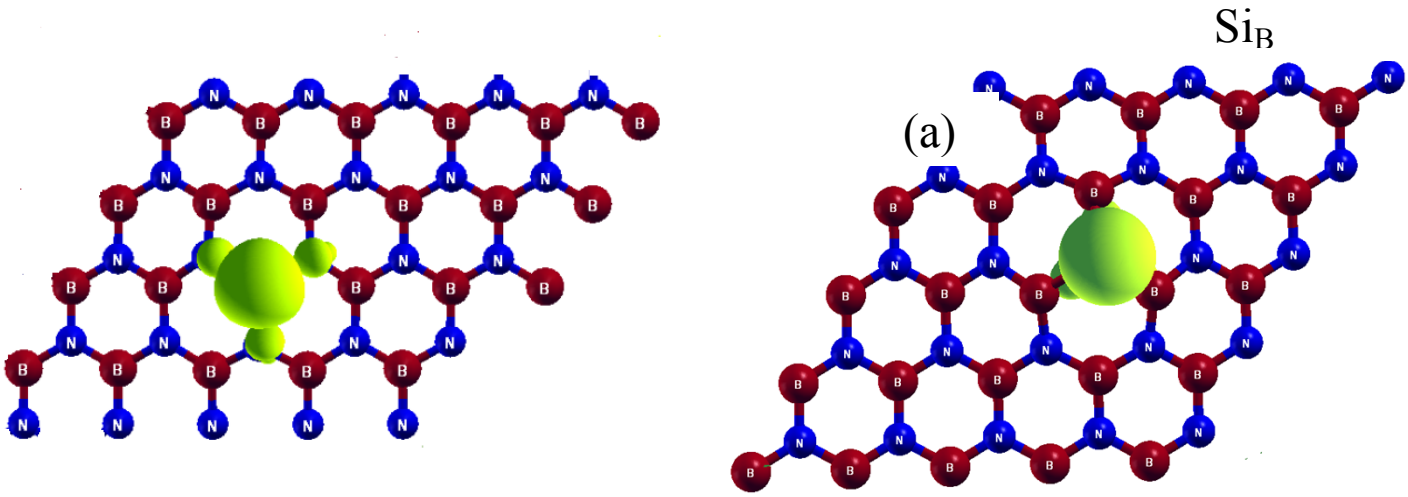

Figure S7: (color online). The spin density contours (1/8th of the maximum value) of Si doped monolayers: (a) Si_B, and (b) Si_N.

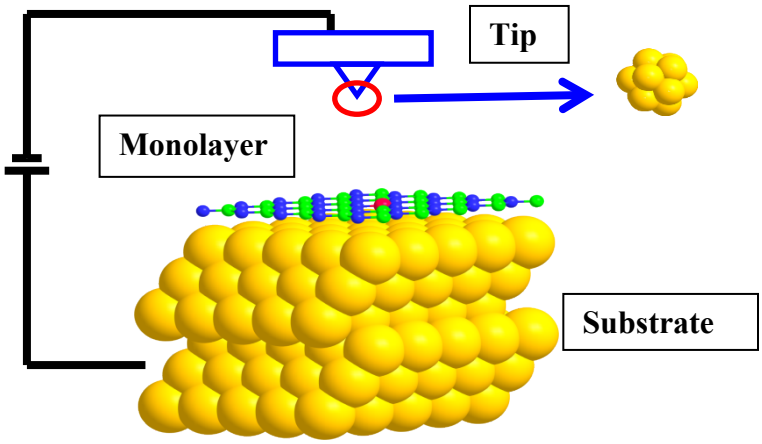

Figure S8: (color online) A schematic illustration of the model STM setup for calculations of the electron transport in the h-BN monolayer deposited on the Au substrate. The cap of the tip is simulated by the Au_{13} cluster.

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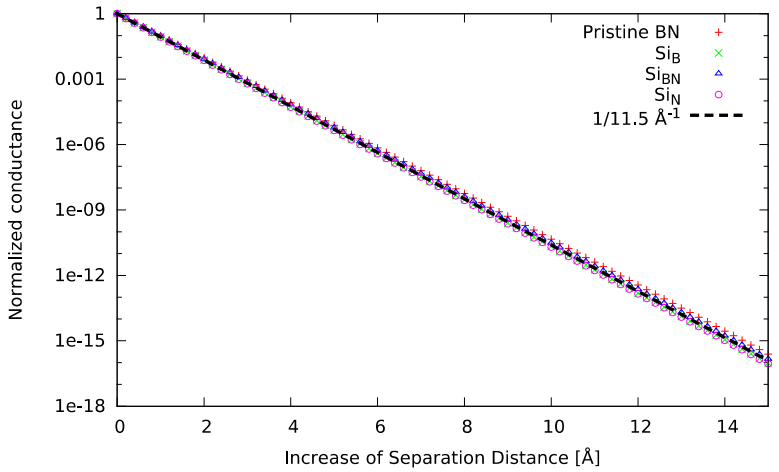

Figure S9: (color online) The variation of the conductance with the tip-sample separation: conductance decreases by a factor of 11.5 per Å as the tip is pulled away from the sample. Normalized conductance is defined as the low-bias conductance at a given distance divided by the conductance at the reference distance, 5 Å from the surface.

Referee 2 -2

The effect of increasing the tip-sample separation (*d*) follows the relationship of exponential decay as established in the Bardeen, Tersoff, and Hamann (BTH) formalism of electron tunneling in the weak-coupling regime. The spin-polarized current is given by:

$$I_{up}(I_{dn}) = \frac{2\pi e}{h}\gamma\int_{-eV/2}^{eV/2}\rho_{s\_up\ (s\_dn)}\left(\varepsilon+\frac{eV}{2}\right)\rho_{t\_up\ (t\_dn)}\left(\varepsilon-\frac{eV}{2}\right)$$
$$\times e^{-2d\sqrt{2(m/\hbar^2)(\phi_{av}-\varepsilon)}}\left\{\left[f\left(\varepsilon-\frac{eV}{2}\right)\right]\left[1-\left[f\left(\varepsilon+\frac{eV}{2}\right)\right]\right]-\left[f\left(\varepsilon+\frac{eV}{2}\right)\right]\left[1-\left[f\left(\varepsilon-\frac{eV}{2}\right)\right]\right]\right\}d\varepsilon$$

(Equation 1)

In our work, the calculated conductance (current) is found to decrease by a factor of 11.5 per Å as the tip separation is increased. In other words, if the tip-sample separation is increased from 5 Å to 10 Å, the current decreases by about 5 orders of magnitude. But the I-V characteristics described in the paper will not be affected.