Supplementary Information//Tuning the Electronic and Magnetic Properties of Antimonene Nanosheet via Point Defects and External Fields: A First-Principles Calculations

Asadollah Bafekry,*,† Mitra Ghergherehchi,*,¶ and Saber Farjami Shayesteh†

†*Department of Physics, University of Guilan, 41335-1914, Rasht, Iran*

‡*Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium.*

¶*College of Electronic and Electrical Engineering, Sungkyun kwan University, Suwon, Korea*

E-mail: Bafekry.asad@gmail.com; mitragh@skku.edu

Computational Methodology

We calculated the electronic structure with different codes including Quantum Espresso, SIESTA and ABINIT. In the PW-basis set with Quantum Espresso, we used kinetic energy cutoffs of 60 Ry and 480 Ry for the wave-functions and charge densities, respectively, and can achieved convergence in the total energy to below 1.0 meV/atom. The convergence for a total energy difference of less than 10^{-6} Ry between two steps and the maximum force allowed on each atom is less than 10^{-3} a.u. between subsequent iterations are chosen as the

convergence tolerance of energy, in the PW basis set with Quantum Expresso code. The calculations with SIESTA where the eigenstates of Kohn-Sham Hamiltonian are expressed as linear combinations of numerical atomic orbitals are performed. The exchange-correlation functional of the GGA-PBE is shown. A 300 Ry mesh cutoff is chosen and the convergence criterion for the density matrix is taken as 10^{-4} Ry.Our first-principles calculations with ABINIT code are conducted in the framework of DFT within the PBE-GGA, and norm-conserving pseudopotentials and the plane-wave cutoff energy of 40 Hartree are used. Both the lattice parameters and the positions of all of the atoms are relaxed until the force is less than 1 meV/Å.

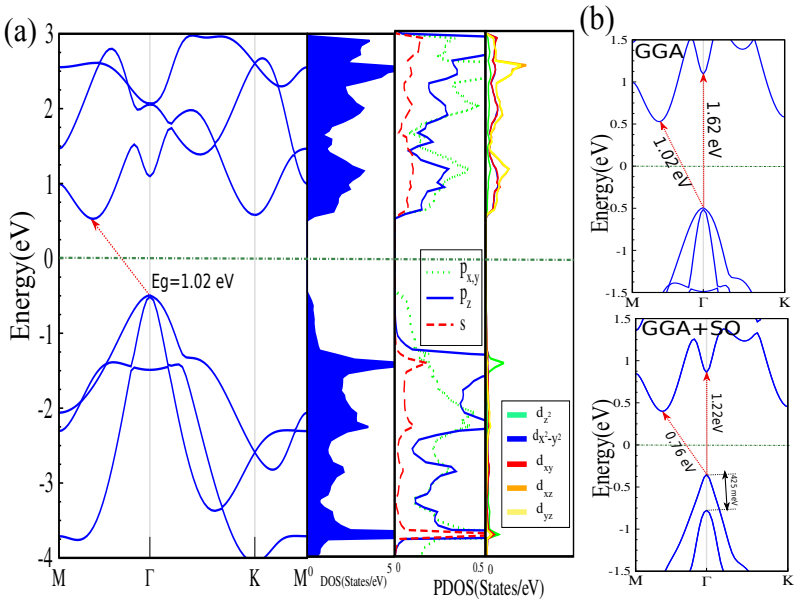

Figure 1: (a) Electronic band structure, densities of states (DOS) and partial density of states (PDOS) of antimonene. (b) Electronic band structure of antimonene without and with spin-orbit coupling (SOC). The zero of energy is set to the Fermi level energy.

The electronic band structure, density of states (DOS), and projected density of states (PDOS) of antimonene are shown in Fig. S1(a). We can see that antimonene is an indirect semiconductor with a 1.02 eV band gap that is located between the valence band maximum (VBM) at Γ and the conduction band minimum (CBM) at M point. This gap decreases to 0.76 eV when the spin-orbit coupling (SOC) is added to the calculation, as shown in Fig. S1(b). From the PDOS of antimonene, we can see that the VBM is dominated by the

Sb-$p_{x,y}$ orbitals, whereas the CBM is dominated by Sb-$p_{x,y,z}$ orbital states. We found that the energy band gap between CB and VB originates from the orbital character of Sb-$p_{x,y}$ states, as shown in Fig. S1(a). When considering relativistic effect of spin-orbit coupling (SOC), it can be seen that the energy degeneracy of certain points in the band structures is broken. The lower branch mainly consists of s-orbitals, while the other two branches are mainly from p-orbitals, thus SOC has a nonzero contribution to p-orbitals, but this vanishes for s-orbitals, because the angular moment of s orbital is zero. As a result, the band gap between the lower branch and the middle branch increases from zero to 42 meV due to the relativistic effect (see Fig. S1(b)). Therefore, SOC influences the middle and upper branches of bands but has no effect on the lower branch.

The optimized structures of the 3d transition metal atoms adsorbed antimonene (TMs/ant) at stable sites, are shown in Fig. S2(a). The difference charge densities of TMs/ant structures are shown in Fig. S2(b). For example, in the Ti/ant, a charge accumulation appears in the region between Ti and the neighboring Sb atoms, which implies the formation of a strongly covalent bond character in the Ti-Sb atoms. This stronger covalent bonding is also found in most of the other TMs/ant.

In order to better identify and investigate the effects of adatom adsorption and defects on antimonene, we simulated their STM images (see Figs. S3(a-h)). Under a bias of +2 V, the structures of the Ad/ant can easily be identified through their STM images. We can see that the Sb atoms appear as white spots however, the regions around H, P, B, and Ti adatoms and different defects correspond with the brighter spots.

In order to investigate the atom substitution on antimonene, we considered the cases in which O, S, F, Cl, N ,P, As, Bi, Li, Na, K, Be, Mg, and Ca atoms replace the Sb host atom of antimonene. Hereafter, the atom substituted on antimonene will be referred to sub-ant. A side view of the optimized structures with corresponding bond lengths between the substituted atom and its nearest Sb atom is shown in Fig. S(4). The difference charge density is shown in the same panel. As can be seen, the bond lengths between the Sb

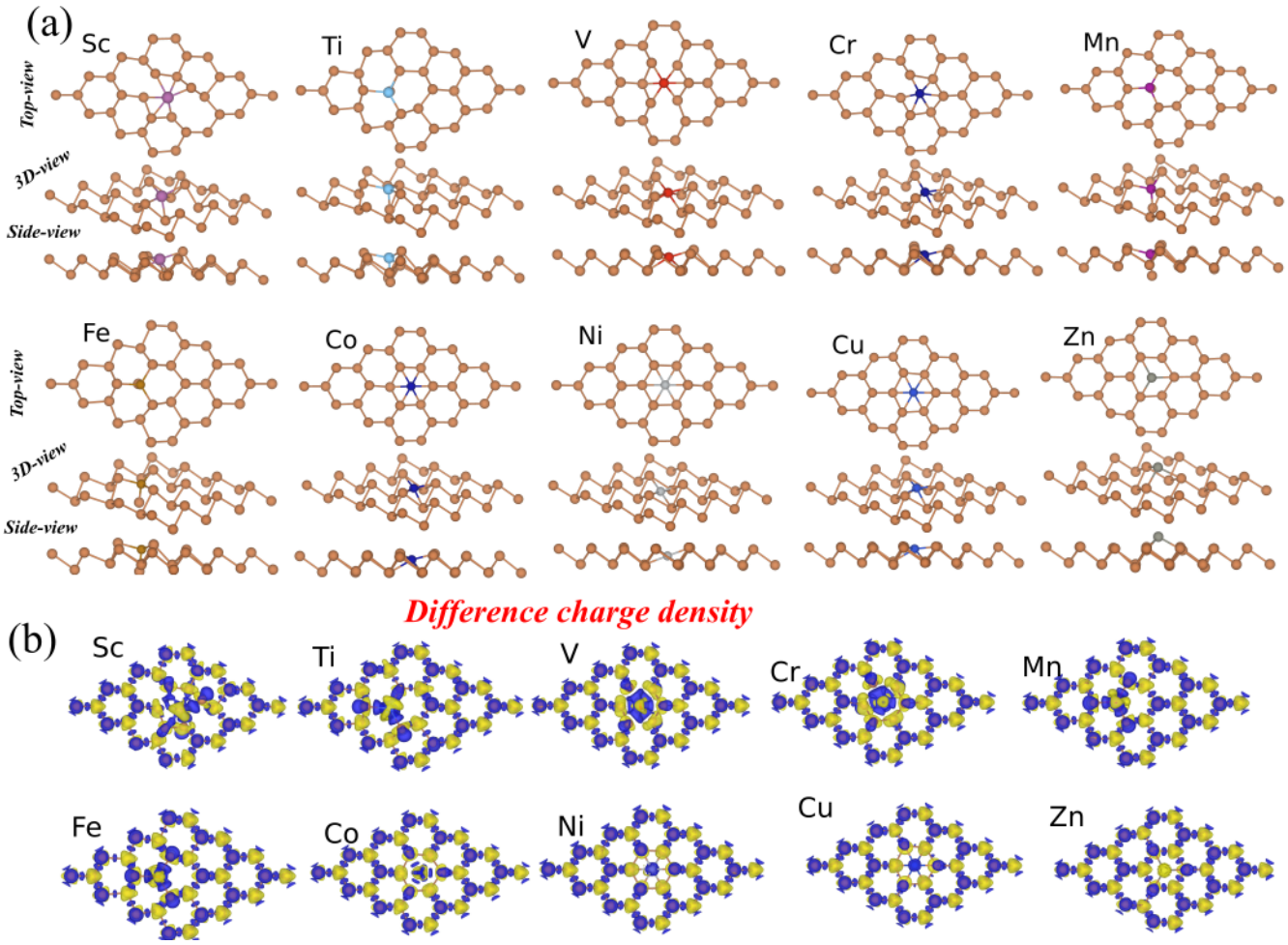

Figure 2: (a) Optimized structures of Ad/Antimonene (Ad= Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Zn adatoms) (b) The difference charge densities. The blue and yellow regions represent the charge accumulation and depletion, respectively.

atom and substituted Be, O, N, P, and S atoms are shorter than the original Sb-Sb bond length, due to the smaller radius and stronger electro-negativities of atoms. The Bi, Na, and K atoms have larger radii and weaker electro-negativity and the bond lengths formed around the Sb atoms are relatively larger. Therefore, after the substitution of these atoms, the antimonene structures have local deformation. The difference charge density of atoms substituted antimonene are shown in the same panel in Fig. S4.

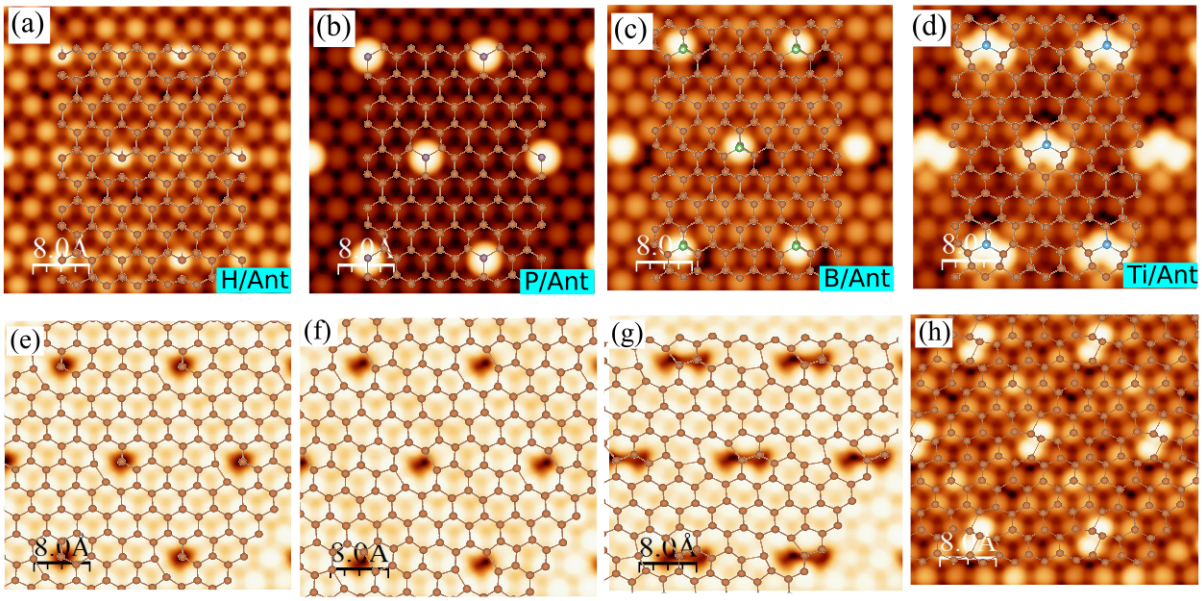

Figure 3: (a) The simulated STM images of Ad/ant (Ad= H, B, Li and Ti). A ball-and-stick model of the antimonene with a adatom is inset to the simulated STM images. The simulated STM images of (e) single vacancy (f,g) double vacancy (h) StoneWales defects on antimonene. A ball-and-stick model of the antimonene is inset to the simulated STM images.

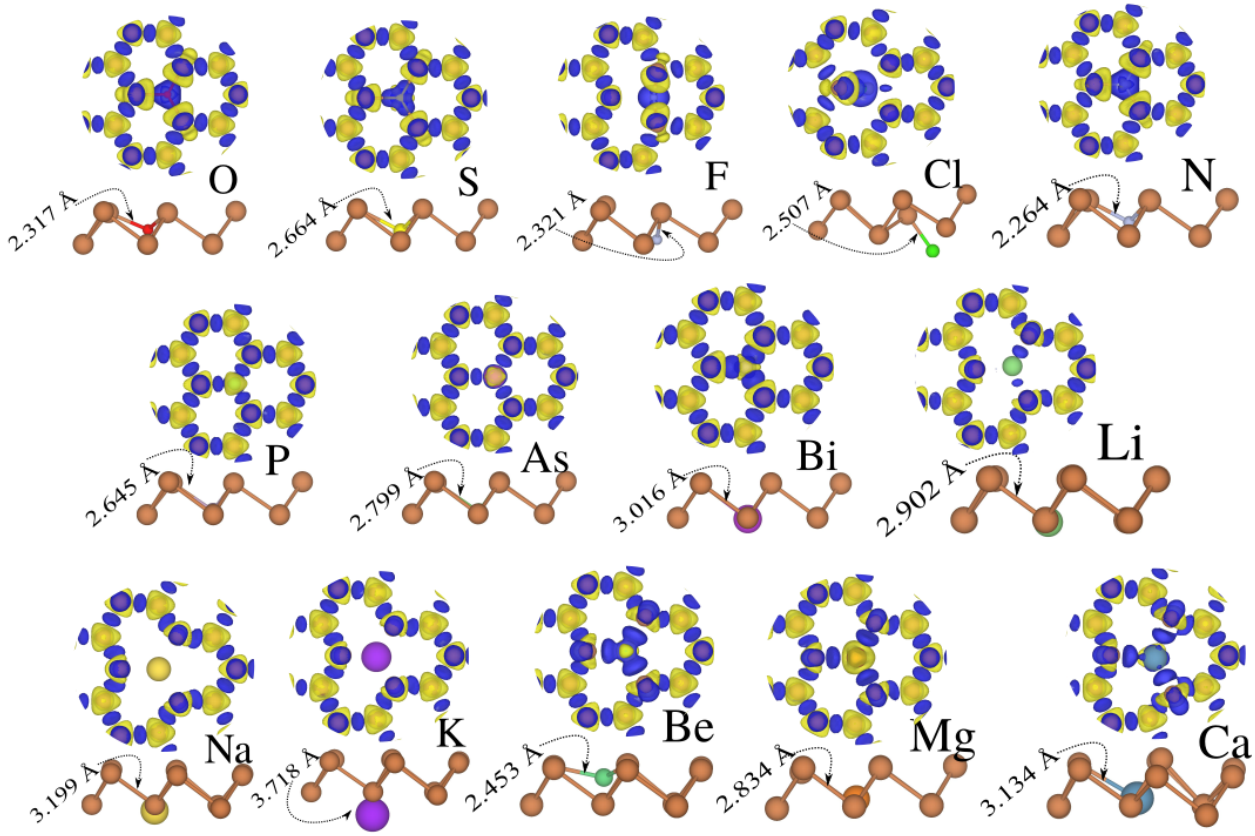

Figure 4: (a) Electronic structure of O, S, F, Cl, N , P, As, Bi, Li, Na, K, Be, Mg and Ca atoms substituted with Sb atom of antimonene. The insets are top view of optimized structures. The zero of energy is set to the E_F.