



Electron affinity and ionization potential of two-dimensional honeycomb sheets: A first principle study



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ABSTRACT

We perform first principle calculations based on density functional theory to study the electron affinity and ionization potential of two-dimensional structures of carbon family, group-III-nitride family and transition-metal dichalcogenide family. We found and explained the atomic number dependence of electron affinity and ionization potential.

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1. Introduction

Graphene has demonstrated the stability of the novel two-dimensional (2D) honeycomb lattice structure [1,2]. However, the gapless energy band near the Fermi level makes it difficult for the applications in devices. Thus, in recent years, many groups pay more attentions to other similar 2D materials [3–7].

Among them, in the case of group IV elements, the graphene-like counterpart of silicon (Si), germanium (Ge) and stannum (Sn) is called silicene, germanene and stanene, respectively. Cahangirov [8] suggested that the low-buckled honeycomb of Si and Ge is stable. The calculations done by Houssa [9] have demonstrated that silicene can behave like graphene. Further experiments have been done by Vogt et al. [10], and Xu [11] who investigated 2D stannum films and found such films are quantum spin Hall (QSH) insulators with sizable bulk gaps of 0.3 eV. Das [12] presented calculations to show that cyclopentadienyl, adsorbed to Si and Ge surfaces, can exhibit spinning motion.

The group-III-nitride (boron nitride (BN), aluminum nitride (AlN), gallium nitride (GaN) and Indium nitride (InN)) are very important materials in applications. The lattice mismatch between graphene and honeycomb BN is less than 2%. So the honeycomb BN could be ideal substrate for graphene [13], which can induce band gap in graphene. Many research groups have investigated the defects [14] and transition-metal doped 2D honeycomb AlN sheet or ribbon [15–17], and demonstrated the stability of infinite honeycomb structure of AlN by DFT calculations. Tang [18] have found that the surface effect, edge effects, and quantum size effect are

three important factors that alter the electronic properties of GaN nanoribbons.

Another serial of important semiconductor is transition-metal dichalcogenide (TMX₂, TM = Mo, W, etc.; X = S, Se, etc.), which are potential materials for field effect transistor (FET) [19,20]. Although the bulk materials of them are indirect-gap, the monolayers of them are direct-gap [21], which makes them more attractive. Recently, obtaining single-layered MoS₂ by mechanical exfoliation of multi-layered MoS₂ [22], the preparation of large-area graphene/MoS₂ heterostructures [23] and the synthesis of a composite-layered MoS₂ nanoflakes [24] became possible. It was reported that the FETs based on MoS₂ via chemical vapor deposition (CVD) exhibited n-type behaviors with electron mobility up to 6 cm² V⁻¹ s⁻¹ [20].

The work function (WF), electron affinity (EA) and ionization potential (IP) affect the band lineup at the heterostructures, which is important for device performance, and thus are key parameters in band engineering [25–27]. The work function of graphene is as large as graphite, around 4.56 eV [28,29]. Shi [30] demonstrated that graphene films can be used as thin transparent electrodes with tunable WF via chemical doping. Yu [31] reported tuning the graphene WF by electric field, and other groups have investigated the WF of carbon nanotube [32,33]. There is no complete study of EA and IP of these emerging 2D structures. This Letter reports the EA and IP (for semiconducting materials) of 2D honeycomb structure of carbon family (silicon, germanium and stannum), group-III-nitride family (boron nitride, aluminum nitride, gallium nitride and Indium nitride) and transition-metal dichalcogenide family (molybdenum disulfide, tungsten disulfide, molybdenum diselenide and tungsten diselenide). The WF of graphene is also listed for comparison. We have also calculated the phonon dispersion with linear response method, which demonstrated the stability of monolayer honeycomb structure of group III-nitride.

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2. Calculation method

First principle calculations based on density functional theory were performed with Vienna ab initio simulation package [34], using the projector-augmented-wave (PAW) potential. The exchange–correlation functional was treated using the Perdew–Wang91 (PW91) [35] generalized gradient approximation (GGA), Perdew–Burke–Ernzerhof (PBE) [36] GGA and Ceperly–Alder (CA) [37] local density approximation (LDA) [38], respectively. An energy cutoff of 500 eV was used in all calculations. The structure optimization was carried out until the forces on atoms fell below 0.001 eV/Å. The electronic convergence tolerance was set to 10^{-6} eV. Monkhorst–Pack Γ -centered k grid of $9 \times 9 \times 1$ and $31 \times 31 \times 1$ were used in optimization and static calculations, respectively. Vacuum slabs of 3.5 nm thick are inserted between neighboring 2D atom sheets. The WF, EA and IP are defined as $WF = \phi - \varepsilon_F$, $EA = \phi - \varepsilon_C$ and $IP = \phi - \varepsilon_V$, respectively, where ϕ is the vacuum level, ε_F is the Fermi level, ε_C is the conduction band minimum and ε_V is the valence band maximum. Usually the Fermi level locates between the valence band and the conduction band depending on the doping and the surface states. The vacuum level ϕ is determined from the potential in the vacuum slab where ϕ approaches a constant.

3. Monolayers of group IV elements

It is reported that a low buckled configuration (Figure 1a) is essential for the stability of silicene (0.44 angstrom buckled displacement) [6,8,39], germanene (0.64 angstrom buckled displacement) [40] and stanene (0.86 angstrom buckled displacement) [41] except for graphene. In our calculations, the buckled displacements are found to be 0.45, 0.68, and 0.85 angstrom for silicene, germanene, and stanene, respectively. The phonon dispersion calculations show such configurations are stable [8,11].

The orbitals of planar graphene are sp^2 hybridization with the bond angles exactly 120° . The bond angles of silicene, germanene and stanene were found to be between 111.2° and 116.4° (Figure 1b), which means that they are not pure sp^2 hybridization, nor pure sp^3 hybridization, but the sp^2/sp^3 mixed hybridization. The bond angle of silicene is consistent with Ref. [42]. The bond angle decreases with the atomic number from Si to Sn. The projected

density of states (PDOS) in Figure 2 indicates that the π bands (those states near the Fermi level) of graphene consist of only p_z orbitals, while those states near the Fermi level of silicene, germanene and stanene consist of other s and p orbitals which means the sp^2/sp^3 mixed hybridization. The sp^2/sp^3 mixed hybridization results in the buckled configuration.

Table 1 lists the WF, IP and EA we obtained comparing with the results in literature. The IP and EA decreases for larger atoms with the increase of bond length and the decrease of bond angle from silicene to stanene. The system turns from sp^2 hybridization into sp^2/sp^3 mixed hybridization for larger atoms, which leaves one dangling bond for each atom in a honeycomb structure, which lifts the energy of the whole system, and thus lowers the IP and EA.

The band structures of monolayer of group IV elements are shown in Figure 3. The bands near the Fermi level cross linearly at K point if the spin–orbital coupling is turned off. The spin–orbital coupling opens a gap. The gap is largest for stanene which is about 0.1 eV. The gap of stanene is close to Xu's result [11].

4. Monolayer honeycomb structure of group III-nitride

The group III-nitride semiconductors are important materials [43–45]. AlN (6.2 eV) and GaN (3.4 eV) are wide gap [46,47] semiconductors, which are suitable for high temperature/high power electronic devices [47–50]. Hexagonal BN (h -BN) has the layered structure similar to that of graphene, which makes it a suitable substrate for graphene [13,45]. So the 2D monolayer of group III-nitride materials are worth a detailed study for both theory and practical applications. Figure 4 shows the phonon dispersion of monolayer honeycomb structure of BN, AlN, GaN, and InN. The result of BN agrees with Ref. [71]. There are three acoustical modes and three optical modes. One optical mode separates from the other two optical modes, and the separated gap gets larger for heavier atom mass. It is clear that the lowest-optical mode represents the relative movement of atoms in direction perpendicular to the atom plane. What is important is that there are no imaginary modes in all phonon dispersions, which makes us believe that the monolayer honeycomb structure is stable. A question is that why the monolayer group III-nitride does not have the buckled configuration. It is because that the nitrogen atoms are negatively charged and thus repel each other. The distance is largest in honeycomb

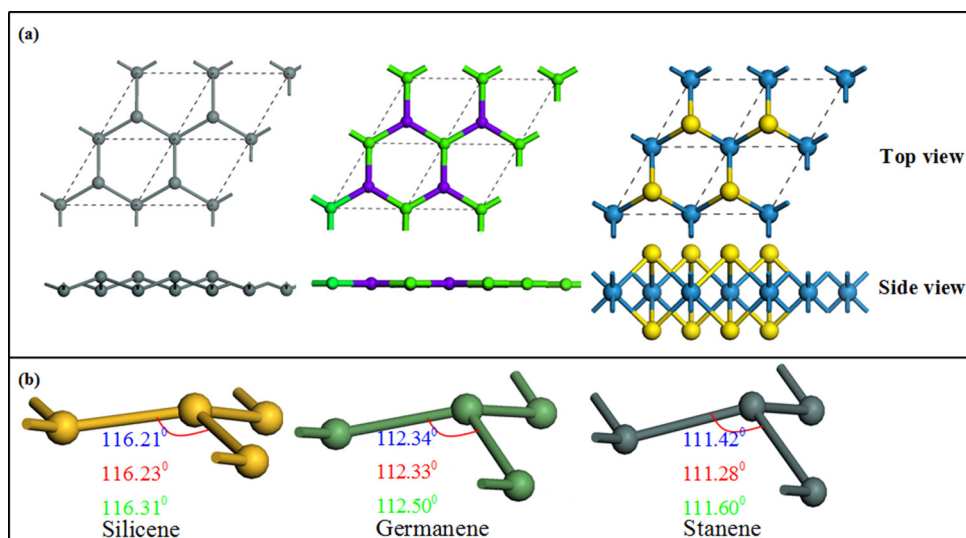


Figure 1. (a) Top view and side view of 2D honeycomb structure of carbon family (left panels), group III-nitride family (middle panels) and the triple layered transition-metal dichalcogenide family (right panels). The atoms in the middle layer in the side view of right panel are Mo or W atoms. (b) Buckled structure of silicene, germanene and stanene. The blue, red and green digits (from top to bottom) are the bond angles obtained with PW91, PBE and CA method respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

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