

INVESTIGATION OF NEW POLYMORPHS OF BOROPHENE AND THEIR FUNCTIONALIZATION

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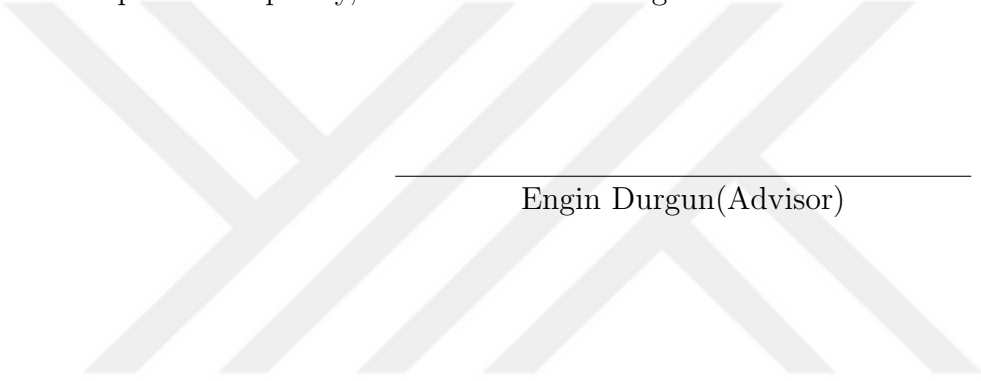
By
Jamoliddin Khanifaev
December 2017

Investigation of new polymorphs of borophene and their functionalization

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We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.



Engin Durgun(Advisor)

Handan Olğar

Serkan Kasırga

Approved for the Graduate School of Engineering and Science:

Ezhan Karaşan
Director of the Graduate School

ABSTRACT

INVESTIGATION OF NEW POLYMORPHS OF BOROPHENE AND THEIR FUNCTIONALIZATION

Jamoliddin Khanifaev

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Advisor: Engin Durgun

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The realization of buckled monolayer sheets of boron (i.e., borophene) and its other polymorphs has attracted significant interest in the field of two-dimensional systems. Motivated by their chameleonic behavior we analyzed different polymorphs of borophene and discovered two new phases with unprecedented crystal structures namely symmetric washboard and asymmetric washboard using *ab initio* methods based on density functional theory. While symmetric washboard borophene is a metal with high electronic density of states in the vicinity of Fermi level asymmetric washboard borophene is a narrow band gap semiconductor. Asymmetric washboard structure is actually a 2×1 reconstructed form of symmetric structure with in plane and out of plane Peierl's distortion along the chains of boron atoms which is the key reason for the contrasting electronic behavior of these phases. Phonons dispersion calculations based on density functional perturbation theory reveal that both structures are stable at 0 K however *ab initio* molecular dynamics simulations showed that symmetric washboard structure is stable only at temperatures close to absolute zero and at finite temperatures this structure gets deformed transforming into asymmetric washboard structure. Moreover we discovered that asymmetric washboard structure has a positive Poisson's ratio however symmetric one has a negative Poisson's ratio. In the next work, motivated by buckled borophene's tendency to donate electrons, we analyzed the interaction of single halogen atoms (F, Cl, Br, I) with borophene. The possible adsorption sites are tested and the top of the boron atom is found as the ground state configuration. The nature of bonding and strong chemical interaction is revealed by using projected density of states and charge difference analysis. The migration of single halogen atoms on the surface of borophene is analyzed and high diffusion barriers that decrease with atomic size are obtained. The metallicity of borophene is preserved upon adsorption but anisotropy in electrical conductivity is altered. The variation of adsorption and formation energy,

interatomic distance, charge transfer, diffusion barriers, and bonding character with the type of halogen atom are explored and trends are revealed. Lastly, the adsorption of halogen molecules (F_2 , Cl_2 , Br_2 , I_2), including the possibility of dissociation, is studied. The obtained results are substantial for fundamental understanding and possible device implementations of borophenes and their halogenated derivatives.



Keywords: density functional theory, DFT, two dimensional materials, borophene, Peierls transition, electronic structure, halogen doping.

ÖZET

BOROFENİN YENİ POLİMORFLARININ ARAŞTIRILMASI VE FONKSİYONELLEŞTİRİLMESİ

Jamoliddin Khanifaev

Malzeme Mühendisliği ve Nanoteknoloji, Yüksek Lisans

Tez Danışmanı: Engin Durgun

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Tek katmanlı bükülmüş boron tabakaları (borofen) ve bunun diğer polimorf yapıları, iki boyutlu sistemlerin bilimsel çalışmalarında büyük ilgi görmüştür. Bu tez çalışmasında, değişken yapısal davranışından dolayı incelediğimiz borofen malzemesinin farklı polimorflarını analiz ettik ve iki yeni kristal yapı fazını ön gördük. Simetrik ve asimetrik kırışık (washboard) olarak adlandırdığımız bu yapıları yoğunluk fonksiyonel teorisine dayanan *ab initio* yöntemlerini kullanarak analiz ettik. Simetrik kırışık borofen, Fermi seviyesi yakınında yüksek elektronik yoğunluklu bir metal gibi davranırken ve asimetrik kırışık borofen dar bant aralıklı bir yarı iletken özellikleri göstermektedir. Asimetrik kırışık yapı aslında simetrik kırışık yapının, bor atomlarının zincirleri boyunca Peierls bozulması ile 2×1 birim hücre olarak yeniden şekillendiği bir fazdır. Bu husus, zıt elektronik davranışlar gösteren fazlara sebep olmuştur. Yoğunluk fonksiyonel pertürbasyon teorisine dayanan fonon dağılım hesaplamaları her iki yapının 0 K'de stabil olduğunu ortaya koymaktadır. Ancak *ab initio* moleküler dinamik simülasyonları, simetrik kırışık geometrinin sadece mutlak sıfıra yakın sıcaklıklarda stabil olduğunu göstermiştir. Normal sıcaklıklarda bu yapı deforme olarak asimetrik kırışık yapısına dönüşür. Ayrıca asimetrik kırışık yapı pozitif bir Poisson sabitine sahipken, simetrik yapının negatif Poisson özelliği gösterdiği bulunmuştur. Ayrıca bu çalışmada, bükülmüş borofenin elektron verme eğilimi göz önünde bulundurularak tek halojen atomlarının (F, Cl, Br, I) borofen ile etkileşimi analiz edildi. Olası soğurma pozisyonları test edildiğinde bor atomunun üst noktası temel durum konfigürasyonu olarak tespit edilmiştir. Bağlanma ve güçlü kimyasal etkileşimin doğası, tahmini durum yoğunluğu ve yük farkı analizleri yapılarak belirlenmiştir. Tek halojen atomunun borofenin üst yüzeyi boyunca hareketi analiz edilmiş ve değişken ama yüksek difüzyon bariyerleri elde edilmiştir. Borofenin metalik özelliği soğurma sebebiyle korunurken elektriksel

iletkenlik anizotropisi deęiřmektedir. Soęurma ve oluřum enerjisinin, atomlar arası mesafenin, yük transferinin, difüzyon bariyerleri ve baęlanma karakterinin halojen atomuna göre deęiřimi arařtırılarak eęilimler ortaya konmuřtur. Son olarak, halojen moleküllerinin (F_2 , Cl_2 , Br_2 , I_2) muhtemel ayrıřmayı ieren soęurması incelenmiřtir. Elde edilen sonular, borofen fazlarının ve halojenli türevleri hakkındaki temel bilginin edinilmesi ve bu malzemelerin muhtemel yüksek teknoloji cihaz uygulamaları iin önemlidir.



Anahtar sözcükler: Yoęunluk fonksiyonel teorisi, iki boyutlu malzemeler, borofen, Peierls bozulması, elektronik daęılım, halojen adsorpsiyonu.

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Chapter 1

Introduction synthesized for the first time

In 2004 Konstantin Novoselov and Andre Geim were awarded the Nobel Prize for groundbreaking experiments regarding two-dimensional material graphene. In graphene, carbon atoms create an in plane network of σ bonds formed by sp^2 hybrid orbitals and π bonds formed by out of plane p_z orbitals resulting in a planar hexagonal crystal structure as shown in Fig. 1.1 [1]. Graphene is the most studied two-dimensional material due to its ease of synthesis and superior properties over other materials such as high Young's modulus (strongest material ever tested), optical transparency, excellent thermal conductivity and high mobility of charge carriers because of the massless Dirac fermions which originate from the out of plane p_z orbitals.

Following the synthesis of graphene [2], immense amount of research has been conducted in the field of two dimensional (2D) materials. Since then various elemental 2D materials including silicene [3], germanene [4], stanene [5] in Group IV, and phosphorene [6], antimonene [7], bismuthene [8] in Group V were realized experimentally and also investigated in detail by advanced computational methods. The ground state bulk form of carbon is graphite (vertical stack of graphene sheets) whereas for silicon it is a diamond-type tetrahedral structure with sp^3

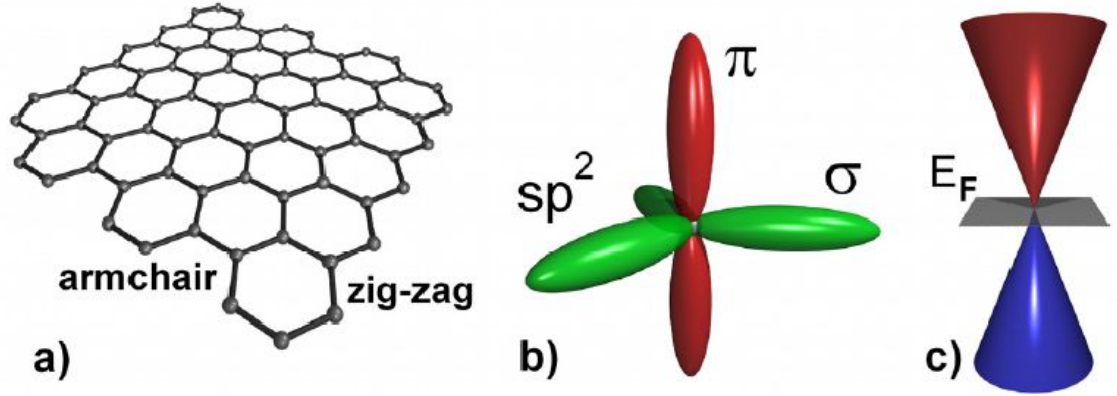


Figure 1.1: Graphene geometry, bonding, and a related band diagram [1].

bonds. Therefore silicene (2D silicon sheet) would have a tendency to form sp^3 type bonding [9]. Indeed it was proven by Cahangirov *et al.* that non-planar buckled configuration is the stable structure of silicene Fig. 1.2[10]. Silicene is also a semi-metal with graphene-like Dirac fermions. However the properties of silicene deviate from graphene due to lower symmetry of the structure and higher mass of Si. These can possibly lead to spin-orbit coupling, non-trivial electronic states and spin-polarized edge states [11, 12, 13]. However monolayer silicon is not stable under ambient conditions due to the reactivity of silicon [14] therefore many attempts to stabilize the structure using various functionalization routes such as hydrogen, oxygen and chlorine passivation were reported [15, 16, 17]. Chemical functionalization was proven to be an effective technique to stabilize the sheet at ambient conditions however further characterization is required to fully understand the effect of surface passivation on the properties of silicene.

Germanene is predicted to form the structure similar to that of silicene with buckled honeycomb configuration Fig. 1.2[18]. Monolayer sheets of germanium are expected to have properties similar to silicene but with enhanced spin-orbit coupling, due to the higher mass of Ge, resulting in stronger topological insulator properties compared to silicene [11, 19]. Halogenation of germanene may enhance its topological insulator properties even further [20]. Chemically modified derivatives such as hydrogen-terminated and methyl-terminated germanene provide enhanced stability and tunable electronic properties [21, 22].

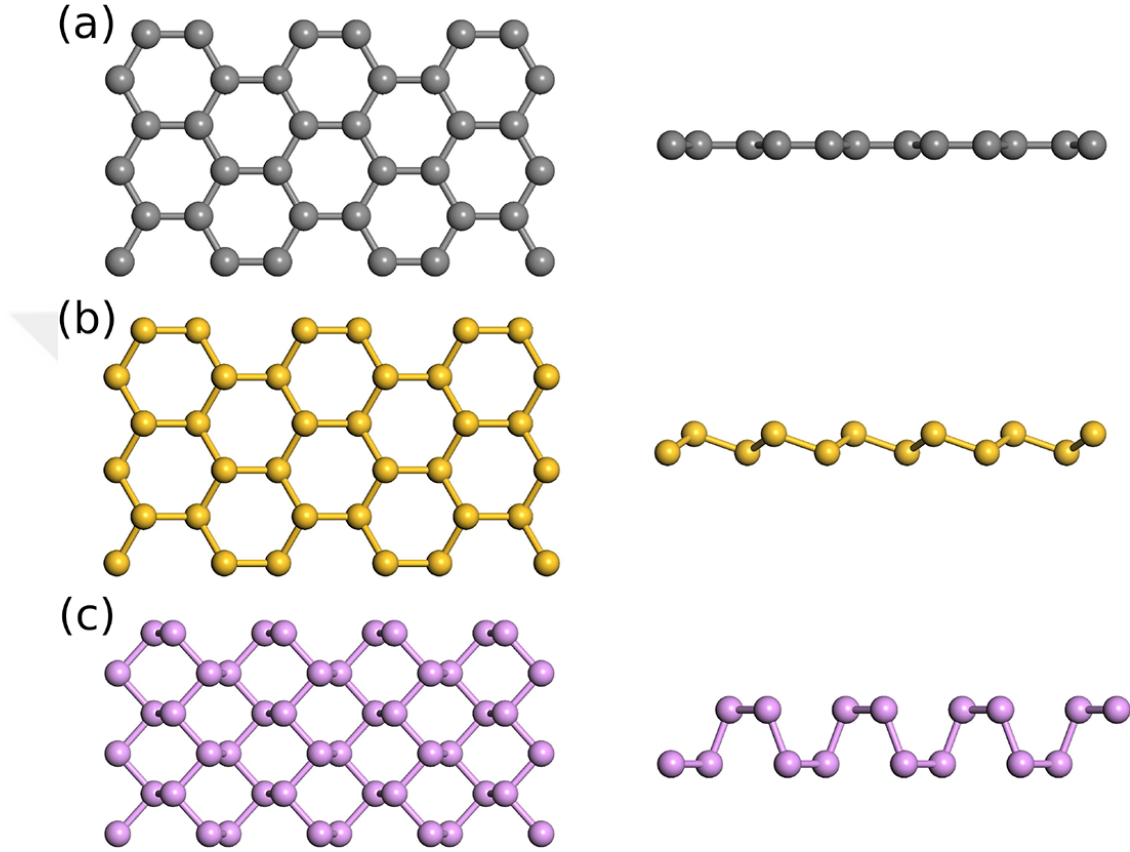


Figure 1.2: Comparison of the crystal structures (top view and side view) among (a) graphene, (b) silicene/germanene/stanene, and (c) phosphorene. Graphene possesses perfect planar structure, silicene possesses low buckling structure, and phosphorene possesses puckered (hinge-like) structure [9].

Two-dimensional allotrope of tin, so called stanene also possesses silicene-like buckled honeycomb structure Fig. 1.2. Tin is even heavier than germanium therefore spin-orbit coupling effects should play very significant role. Indeed it was shown that topologically nontrivial states originating from spin-orbit coupling cause the opening of the band gap around 0.1 eV [23]. These features make stanene a very promising material for spintronic applications. The stability of stanene sheets has not been investigated in detail yet but unsaturated p_z orbitals within the sheet imply high reactivity of the stanene. Therefore proper functionalization of stanene for stabilization and tunability of properties is also of primary

importance. Magnetic dopants are especially interesting because they can lead to chemical engineering of topologically non-trivial states which in turn can result in quantum computing application [24].

Phosphorene has been predicted to form several distinct allotropes based on the degree and scheme of buckling [25]. The most well known polymorph of phosphorene is so called black phosphorus. It forms a puckered structure with considerable degree of corrugation Fig. 1.2 which results in anisotropy in terms mechanical, electronic and optical properties [26]. Very recently another polymorph of phosphorene, with buckled honeycomb configuration similar to that of silicene and germanene, was grown using ultra-high vacuum molecular beam epitaxy (UHV MBE) which is named as blue phosphorus [27]. Both of the synthesized allotropes exhibit semiconducting electronic properties [28, 27]. Phosphorene easily oxidizes when exposed to air therefore it is hard to obtain and process pure monolayer sheets under ambient conditions [29]. Similar to the case of previously discussed 2D materials functionalization of phosphorene is of a significant importance. It was shown that functionalization of phosphorene using diazonium salts creates a stable passivation layer on the surface of the sheet inducing a p-type doping and enhanced ambient stability [30].

Antimony and bismuth have layered 3D structures [33]. Both antimonene and bismuthene have two allotropes which have buckled honeycomb and puckered (washboard) structures in Fig. 1.2. Due to the large mass of Sb and Bi strong spin-orbit coupling and its effect on the properties of monolayers is expected. Interestingly both materials are predicted to be narrow band gap semiconductors and by increasing number of layers their band gaps close [34, 35].

The synthesis of borophene [32, 36], monoatomic lattice of boron atoms, has extended this family to Group III elements. Boron is a light element which is located at the boundary between metals and nonmetals in the periodic table and has rich chemistry. Due to its electron shell configuration ($[\text{He}] 2s^2 2p^1$) and flexibility to adopt various hybridizations, it can form complex bondings ranging from two-center-two electron to seven-center-two electron bonds [37]. This results in variety of boron allotropes, which can be found in all-dimensions with diverse

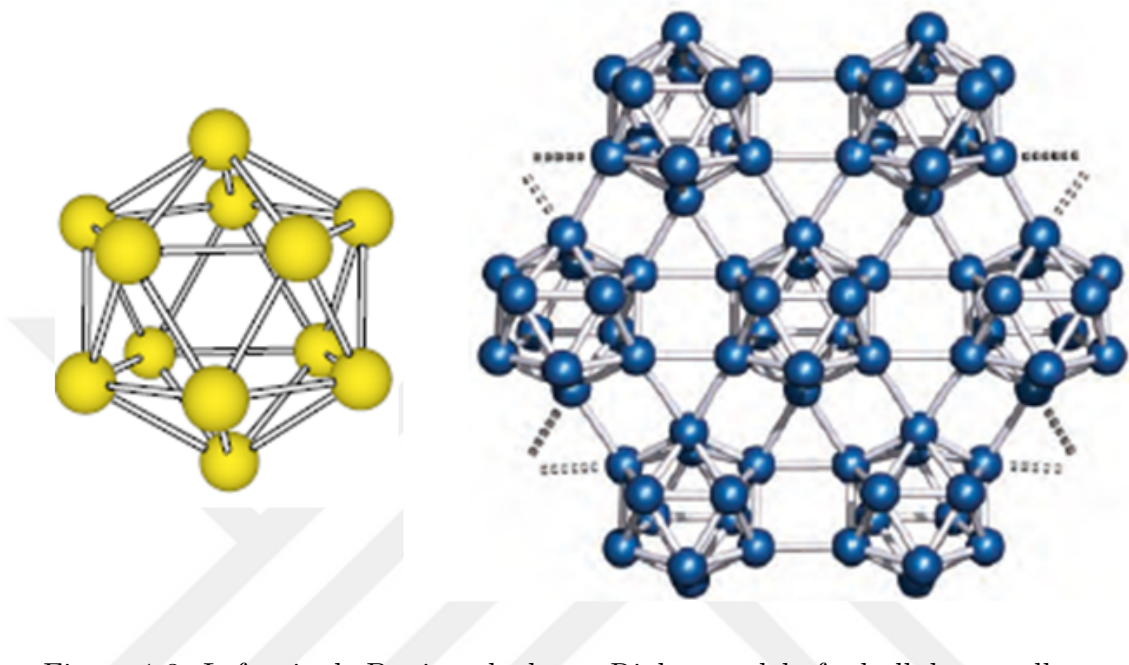


Figure 1.3: Left: single B₁₂ icosahedron ; Right: model of a bulk boron allotrope which consists of the B₁₂ [31].

chemical and physical properties [38, 39, 40, 41, 42]. All reported bulk boron forms consist of the common building block so called B₁₂ icosahedra Fig. 1.3 . The bonding within icosahedra is of three-center-two electron type whereas the bonding between icosahedra is of the two-center-two-electron type [43]. Such mixture of different types of bonding is also common in low-dimensional boron systems which is the actual cause of polymorphism of low dimensional boron systems.

In addition to various low-dimensional allotropes, very recently Mannix *et al.* have grown the first atomically thin boron sheet on Ag(111) substrate under ultrahigh-vacuum conditions Fig. 1.4 [32]. It has buckled structure with triangular arrangement belonging to $Pmmn$ space group. Following this work, two planar structures of borophene, namely β_{12} and χ_3 phases [36] were also synthesized. Both β_{12} and χ_3 sheets contain periodic arrangement of holes as shown in Fig. 1.5 which act as scavengers of electrons occupying antibonding bands, thus hexagonal holes improve stability of the borophene and contribute to the planarity of the structure[44]. In addition to those, various stable borophene polymorphs

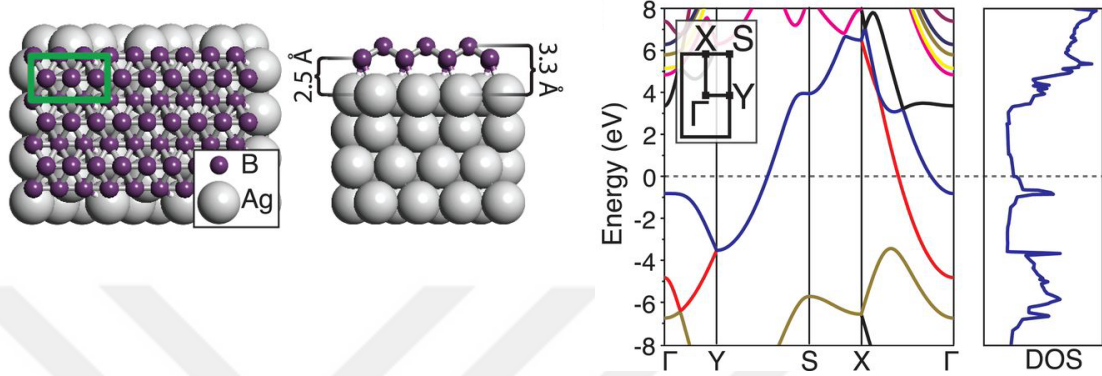


Figure 1.4: Top and side views of the low-energy monolayer structure (unit cell indicated by green box); band structure (inset: 2D Brillouin zone) and DOS for freestanding borophene [32].

with different hole patterns and densities have also been theoretically predicted [39, 45] which may be realized in near future.

Even though all known bulk boron allotropes are semiconductors at ambient conditions, buckled borophene is metallic with highly anisotropic electronic properties [32]. It also possesses mechanical anisotropy where in-plane Young's modulus is equal to 170 GPa.nm along corrugated (zigzag) direction, and 398 GPa.nm along uncorrugated (armchair) direction, which is even higher than that is obtained for graphene (340 GPa.nm) [46]. The structure has negative Poisson's ratio due to the out-of-plane buckling [32] and also significant negative thermal expansion coefficients are reported for both directions [47]. In a theoretical study, large optical anisotropy with high optical transparency and electrical conductivity is reported [48]. Furthermore, a systematic investigation of thermal properties indicates that the thermal conductivity of borophene is also anisotropic and low due to the strong phonon-phonon scattering. The calculated values are $\sim 20 \times 10^{-9} \text{ W.K}^{-1}$ and $\sim 40 \times 10^{-9} \text{ W.K}^{-1}$, along zigzag and armchair directions, respectively [47]. Moreover, experimentally realized borophene sheets are predicted to display intrinsic superconducting behavior at low temperatures [49, 50] which can be enhanced by the tensile strain and hole doping [51].

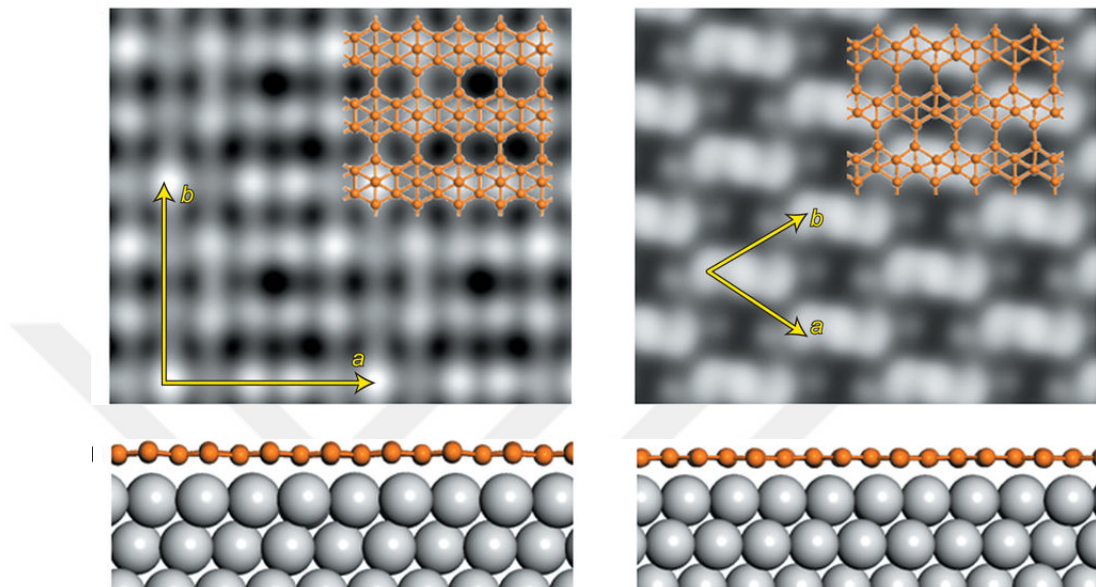


Figure 1.5: Left: simulated STM topographic image of the β_{12} sheet. ; Right: simulated STM topographic image of the χ_3 sheet. Orange and grey balls in represent boron and silver atoms, respectively. The basic vectors of the super cell including the Ag(111) substrate are marked by yellow arrows. Models of the β_{12} and χ_3 sheets are superimposed on their simulated STM images [36].

These properties make borophene an ideal candidate for various applications [36]. Ab initio studies predicted that doped borophene can be used as catalyst for hydrogen and oxygen evolution reactions [52], is a promising anode material for lithium-ion batteries, [53, 54] and is a potential hydrogen storage medium [55]. Boron-based microelectronic device applications is an another interesting field, however the implementation of borophene requires further investigation. This can be possible by functionalization of such systems in order to attain desired properties. Extensive amount of experimental and theoretical work dedicated to the doping of 2D materials prove that it is an effective and progressing technique for tuning the existing properties [56, 57, 58, 59].

In this respect, halogen atoms and molecules are interesting class of adsorbates due to their high electronegativity. They can substantially modify the structural and electronic features of 2D materials upon adsorption or decoration, and they are widely studied both experimentally and theoretically. For instance, fully and

partially fluorinated graphene has already been synthesized [60] and explored in detail [61, 62]. It was shown that fluorine coverage results in band gap opening which can be engineered with degree of fluorination [63]. Moreover, partially chlorinated [64] and brominated [65] graphene derivatives have been reported and the interaction of halogen atoms with graphene is studied by first-principles methods [61, 66, 67, 68]. Not only graphene but also chlorinated silicene [69] and fluorinated boron nitride sheets [70] have also been realized. In addition to experimental efforts, various theoretical studies analyzed the interaction of halogen atoms with 2D systems [71, 72, 73]. It is reported that halogenated 2D materials exhibit remarkable electronic, optical, thermal, mechanical, and chemical properties in comparison with bare counterparts.

Inspired by the chameleonic behavior of boron we questioned if there exist other polymorphs of borophene. Thus we analyzed different geometries of borophene by various optimization methods using Vienna *ab initio* Simulation Package (VASP) and discovered 2 new structures of borophene with novel properties. We named these structures symmetric washboard and asymmetric washboard borophenes. These two polymorphs are structurally very similar but one has slight distortion originating from Peierls instability. Due to Peierls distortion discovered polymorphs of borophene possess different mechanical and electronic properties in the sense that symmetric washboard structure is metallic with a high electronic density of states peak around the Fermi level while the asymmetric washboard structure is a narrow band gap semiconductor. Interestingly these structures can transform into each other upon application of strain along one of the axes. Further details will be discussed in the Results and Discussions part.

In addition to that, we investigated the interaction of single halogen atoms ($X = \text{F, Cl, Br, I}$) with buckled monolayer sheet of boron (which will be referred simply as borophene) using *ab initio* methods. Firstly, we tested all the possible adsorption sites and determined the ground state configurations. The nature of bonding is revealed by projected density of states (PDOS) and charge transfer analyses. The migration of single halogen atom on surface of borophene is studied and diffusion barriers were calculated. The change in the electronic structure is

also examined and compared with pristine borophene. The variation of adsorption energy, interatomic distance, charge transfer, diffusion barriers, and bonding character with type of halogen (i.e up/down in group VII) is explored and trends are revealed. Finally, the adsorption of halogen molecules ($X_2 = F_2, Cl_2, Br_2, I_2$) and the case of dissociation is studied.



Chapter 2

Theoretical background and methodology

2.0.1 Many body problem

Schrödinger equation is the central concept in quantum mechanics. Time independent Schrödinger equation is simple and straightforward which is given as follows :

$$\hat{H}\Psi = E\Psi \tag{2.1}$$

where $\hat{H}$ is so called Hamiltonian operator, Ψ is a wavefunction describing the state of the system and E is the eigenvalue of the $\hat{H}$ which corresponds to the total energy of the system. In principle this equation is able to describe atoms, molecules and even macrosystems. However in order to solve this equation for systems even as small as Li atom, we need huge computational resources due to many body effects. To describe a realistic quantum mechanical systems consideration of many body effects is of primary importance. Hamiltonian operator describing many body systems has the following form:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} \quad (2.2)$$

where $\hat{T}_e$ is the electronic kinetic energy, $\hat{T}_n$ is the nuclear kinetic energy, $\hat{V}_{ee}$ is the electron-electron potential, $\hat{V}_{en}$ is the electron-nuclei potential and $\hat{V}_{nn}$ is the nuclei-nuclei potential. To simplify the problem Born-Oppenheimer approximation was introduced [74], where the main idea is that nuclei move so slow compared to electrons that we can decouple the nuclear and electronic degrees of freedom. Thus Schrödinger equation can be separated into two decoupled forms:

$$\hat{H}_n \psi_i^n(\vec{R}) = E_i^n \psi_i^n(\vec{R}) \quad (2.3)$$

and

$$\hat{H}_e \psi_i^e(\vec{r}) = E_i^e \psi_i^e(\vec{r}) \quad (2.4)$$

Therefore nuclei can be considered as classical particles and electrons are coupled to nuclei only by Coulomb interaction. Due to these approximations problem can be reduced to the Schrödinger equation describing the electrons moving in an electrostatic potential generated by the nuclei.

$$\hat{H} \psi_i(\vec{r}_e) = E_i \psi_i(\vec{r}_e) \quad (2.5)$$

The problem is simplified but this is still a many body problem.

Now, let's consider the Hamiltonian operator after Born-Oppenheimer approximation.

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ext} \quad (2.6)$$

Here $\hat{T}$ is kinetic energy operator of electrons, $\hat{V}$ Coulomb interaction operator between electrons and $\hat{V}_{ext}$ is external potential operator caused by nuclei. Coulomb interaction operator or simply Coulomb potential is given by

$$V = \frac{q}{4\pi\epsilon |\vec{r} - \vec{r}'|} \quad (2.7)$$

where q is the elementary charge of an electron. So the Hamiltonian depends strictly on the external potential, position of an electron and total number of electrons which is still complicated. Hohenberg and Kohn realized that to solve such a complicated formulation it would be more convenient to deal with so called electron density $n(\vec{r})$ [75]. It turned out that it makes the problem simpler while the results remain accurate.

$$n(\vec{r}) = N \int d^3\vec{r}_2 \int d^3\vec{r}_3 \dots \int d^3\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad (2.8)$$

From the above equation we can calculate the total number of electrons because the wavefunction is normalized,

$$N = \int d(\vec{r}) n(\vec{r}) \quad (2.9)$$

2.0.2 Hohenberg and Kohn approach

Hohenberg and Kohn showed that external potential acting on an electron V_{ext} is the functional of the electron density $n_0(\vec{r})$. At first glance this looks very strange because it means that from the ground state density $n_0(\vec{r})$ we can calculate ground state wave function $\psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$, in other words function of one variable is equivalent to the function on N variables. But it turns out that $n_0(\vec{r})$ is a very powerful function which contains enough information to solve quantum mechanical problems of the many body systems. Thus the total energy of the system can be expressed as the functional of charge density

$$E[n(\vec{r})] = T[n(\vec{r})] + V[n(\vec{r})] + V_{ext}[n(\vec{r})] = H_{FK}[n(\vec{r})] + \int d(\vec{r}) V_{ext}(\vec{r}) n(\vec{r}) \quad (2.10)$$

Where $T[n(\vec{r})]$ is the kinetic energy of the electrons, $V[n(\vec{r})]$ is the potential energy of the electrons and $V_{ext}[n(\vec{r})]$ is the external potential energy. Furthermore

Hohenberg and Kohn introduced internal energy functional $H_{FK}[n(\vec{r})]$ which does not depend on V_{ext} and allows to define ground state wavefunction ψ_0 and reproduces ground state density n_0 . In other words energy density functional $E[n]$ has its minimum at the the ground state density n_0 which is essentially the main idea of the density function theory. Due to aforementioned theorems the 3N variable problem of the Schrödinger equation has been reduced into 3 degrees of freedom of $n(\vec{r})$ which drastically simplified the problem and made efficient at the same time accurate quantum mechanical calculations possible.

2.0.3 Kohn-Sham equations

The main problem with the aforementioned approach is that the minimization of H_{FK} is not a very easy task therefore Kohn and Sham came up with a new approach [76] in which they used a special type of single-particle wavefunction which allowed treatment of Schrödinger equation as a single particle problem by including so called exchange-correlation functional takes into account many body effects. To do that they decomposed H_{FK} as shown below

$$H_{FK}[n] = T[n] + V_H[n] + E_{XC}[n] \quad (2.11)$$

where $T[n]$ is the kinetic energy of the non-interacting electron gas, $V_H[n]$ is its Hartree energy and the remaining terms are included in the exchange-correlation energy $E_{XC}[n]$.

$$V_H[n] = \int \int d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (2.12)$$

$$T[n] = -\frac{\hbar^2}{2m} \sum_i \int d^3\vec{r} \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) \quad (2.13)$$

As we can see from the equation, $T[n]$ depends on single-particle wavefunctions of the non-interacting system with charge density n . So $T[n]$ is an explicit functional of ϕ_i but an implicit functional of n , therefore direct minimisation of $E[n]$ with

respect to density n is impossible. To solve this problem Kohn and Sham introduced a new method which minimises the $E[n]$ in an indirect way. In this method they reduced the problem of minimisation of $E[n]$ by solving the single-particle Schrödinger equation for a system consisting of non-interacting particles moving in an effective potential $V_{eff}(\vec{r})$, in this model $V_{eff}(\vec{r})$ includes Hartree energy, exchange-correlation energy and external potential energy:

$$V_{eff}(\vec{r}) = V_H(\vec{r}) + V_{XC}(\vec{r}) + V_{ext}(\vec{r}) \quad (2.14)$$

Thus the wavefunctions that satisfy the single particle Schrödinger equation with V_{eff} will reproduce the exact $n(\vec{r})$ of the original many body problem:

$$\left[-\frac{\hbar^2}{2m} + V_{eff} \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \quad (2.15)$$

$$n(\vec{r}) = n_{eff}(\vec{r}) = \sum_i f_i |\phi_i(\vec{r})|^2 \quad (2.16)$$

where f_i is the partial occupancy of the wavefunction ϕ_i . But the problem is that V_H and V_{XC} depend on n which depends on ϕ_i which in turn depends on V_{eff} , so we are dealing with a closed loop problem. This problem can be solved in an iterative self-consistent manner. We should start with an initial guess of $n(\vec{r})$, which will get us the corresponding $V_{eff}(\vec{r})$ leading to ϕ_i . Following this procedure we get a new charge density and we repeat these cycles until it converges. Once the cycle is converged we can easily obtain the value of the total energy.

2.0.4 Exchange-correlation (XC) approximations : LDA and GGA

Important issue to address is that the exchange-correlation term V_{XC} is not known exactly therefore it has to be approximated. Fortunately adiabatic connection allows us to derive a reasonable approximation for E_{XC} [77, 78].

The main approximations for E_{XC} are the local density approximation (LDA) and the generalized gradient approximation (GGA). The LDA is based on well-known homogenous electron gas, precisely speaking it approximates the E_{XC} by integrating exchange correlation density over all local contributions of homogeneous electron gas. This is a simple model but it gives quite accurate results for structural properties, electronic band structure, phonons dispersion type of calculations even for systems which are different from homogeneous electron gas. Another important approximation is GGA which we used in all of our calculations. While LDA considers only the $n(\vec{r})$ only around specific points GGA takes into account the gradient of E_{XC} . There is a multitude of GGA approximations such as PW91 and PBE functionals [79, 80, 81] which give improved results over LDA, such as ground state energy, binding energies, lattice constants, hydrogen bonds etc. However GGA approximations is still not perfect and it has its own drawbacks such as underestimating bond strengths, band gaps and electrostatic potential above surfaces.

2.0.5 Periodic boundary conditions

For calculation of crystalline materials we need to work with huge number of atoms, therefore Kohn-Sham approximation alone becomes not applicable. Solution is to introduce periodic boundary conditions meaning that we impose translational symmetry. In this type periodic boundary condition electrons move in an external periodic potential $V_{ext}(\vec{r})$ so that

$$V_{ext}(\vec{r} + \vec{R}) = V_{ext}(\vec{r}) \quad (2.17)$$

where periodicity is given by

$$\vec{R} = \sum_i n_i \vec{a}_i \quad (2.18)$$

and

$$V_{uc} = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| \quad (2.19)$$

where $\vec{a}_i$ is a lattice vector of the primitive unit cell with the volume V_{uc} . We need to introduce the reciprocal lattice vector $\vec{G}$ so that $\vec{R} \cdot \vec{G} = 2\pi n$ which will

allow us to represent the lattice periodic functions using Fourier transforms:

$$f(\vec{r}) = \frac{1}{\sqrt{V_{uc}}} \sum_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} f(\vec{G}), f(\vec{G}) = \frac{1}{\sqrt{V_{uc}}} \int_{V_{uc}} d^3\vec{r} e^{-i\vec{G}\cdot\vec{r}} f(\vec{r}) \quad (2.20)$$

This Fourier transform shows us that reciprocal vector $\vec{G}$ has the same periodicity as real lattice vector $\vec{R}$ so that analog of Wigner-Seitz unit cell of real space in reciprocal space which is called Brillouin zone. This means that any V_{ext} will also satisfy the periodic boundary condition. According to Bloch's theorem any wavefunction of such periodic lattice has to satisfy the condition[82]

$$\phi_{n\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{r}\cdot\vec{R}} \phi_{n\vec{k}}(\vec{r}) \quad (2.21)$$

where $\vec{k}$ is an arbitrary vector in reciprocal space. The charge density $n(\vec{G})$ can be obtained by expansion of coefficient of the Fourier transform $c_{n\vec{k}}(\vec{G})$

$$n(\vec{G}) = \frac{2}{\sqrt{V}} \sum_{n,\vec{k}} \sum_{\vec{G}'} c_{n,\vec{k}}^*(\vec{G}^*) c_{n,\vec{k}}(\vec{G} + \vec{G}') \quad (2.22)$$

expansion coefficients $c_{n,\vec{k}}(\vec{G})$ can be obtained by diagonalizing the Hamiltonian $\hat{H}_{\vec{G}+\vec{k},\vec{G}'+\vec{k}}$. In a real calculation the sum over $\vec{G}$ has to be reduced to

$$\frac{\hbar^2}{2m} |\vec{k}^2 + \vec{G}^2| \leq E_{cut} \quad (2.23)$$

Thus the size of the plane-wave basis set is controlled by E_{cut} . Now everything looks fine but one problem is still not solved. The plane-wave basis set describes the wavefunction between atoms pretty accurately however when we deal with the region near nuclei we are facing a problem due to fluctuations and oscillations of the wavefunction. But thankfully the inner core electrons which are located near the nuclei do not play much role in forming interatomic bonds. Therefore we can state that mainly valence electrons contribute to the structural, electronic and phononic properties of the systems. Accordingly, we require a new approximation by introducing a so called pseudopotential concept. The essential meaning of pseudopotential lies in the idea that core electrons and the shape of the valence orbitals are insignificant for determining the physical and chemical properties of the system of interest. The most well-known approach is a projector-augmented wave pseudopotential (PAW) [83] in which the bonding is formed mainly by outer

shell electrons thus the properties of the system are calculated by plane basis set expansion and near core wavefunctions are approximated by radial projector functions. In this way we can get very accurate results without spending excessive computational resources.

2.0.6 Computational Details

In this thesis, we performed ground-state total energy and electronic structure calculations by first-principles methods based on density functional theory (DFT) [84, 85]. The electron exchange and correlation potential is described by the generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) form [86]. All atomic positions are optimized by minimizing the total energy and atomic forces using the conjugate gradient method by setting energy and force convergence to 10^{-5} eV and 10^{-2} eV/Å, respectively. In the project related to novel polymorphs of borophene the projector augmented-wave potentials (PAW) [87, 88] with an energy cutoff at 420 eV was used as implemented in the Vienna ab initio simulation package (VASP) [89, 90]. Monkhorst-Pack $28 \times 18 \times 1$ mesh grid sampling was used for the Brillouinzone integrations of the primitive unit cell. A supercell geometry with a vacuum space of 15 Å in the z direction was adopted to avoid spurious interactions between the periodic images, a supercell with vacuum space was adopted. In addition, ab initio phonon calculations and thermal stability of the structures were tested at high temperatures by ab initio molecular dynamics (MD) calculations.

In the project related to the interaction of halogens with borophene PAW with an energy cutoff at 520 eV was used. Bader analysis was implemented [91] to quantify the charge exchange between the X atoms and the borophene. To avoid interactions between dopants, 7×4 supercell was used with lattice constants, 11.45 Å and 11.30 Å in x and y directions, respectively, and 15 Å vacuum space was adopted in the non-periodic z-direction. The Brillouin zone (BZ) was sampled by Γ -centered 6×6 k-point mesh grid [92].

The adsorption (or binding) and formation energies of halogen atoms were

obtained by using the formulas:

$$E_b = E_T(\text{Borophene}) + E_T(\text{X}) - E_T(\text{Borophene+X}) \quad (2.24)$$

and

$$E_f = E_T(\text{Borophene}) + E_T(\text{X}_2)/2 - E_T(\text{Borophene+X}) \quad (2.25)$$

where $E_T(\text{Borophene})$, $E_T(\text{X})$, $E_T(\text{X}_2)$, $E_T(\text{Borophene+X})$ is the total energy of pristine borophene, free X atom, X_2 molecule and doped system, respectively [93, 94]. All energies are calculated by using the same supercell size and identical parameters. Positive value of E_b implies that adsorption is energetically favorable. The diffusion path calculations were performed using the nudged-elastic band (NEB) approach where intermediate images along the reaction path is optimized while equal spacing to neighboring images is maintained [95, 96].

2.0.7 Nudged elastic band approach

Nudged elastic band method (NEB) is based on an idea in which we interpolate the number images of the geometrical configurations between the initial and final states of the system. These images are connected by imaginary elastic springs. If we set N images in total we would have $N+1$ images including initial and final configurations. Imaginary elastic spring forces act in the direction tangent to the path of the reaction while real forces could act in any direction. This way we can get the curves of the energetic barriers during reaction.

2.0.8 Peierls transition

Rudolf Peierls proved that a hypothetical one-dimensional metal at $T = 0$ K will spontaneously get deformed due to electron-phonon interactions or charge density waves (CDW) Fig. 2.1 [97]. This deformation is energetically favorable and it will result in band folding in the Brillouin zone, which in turn will create a band gap

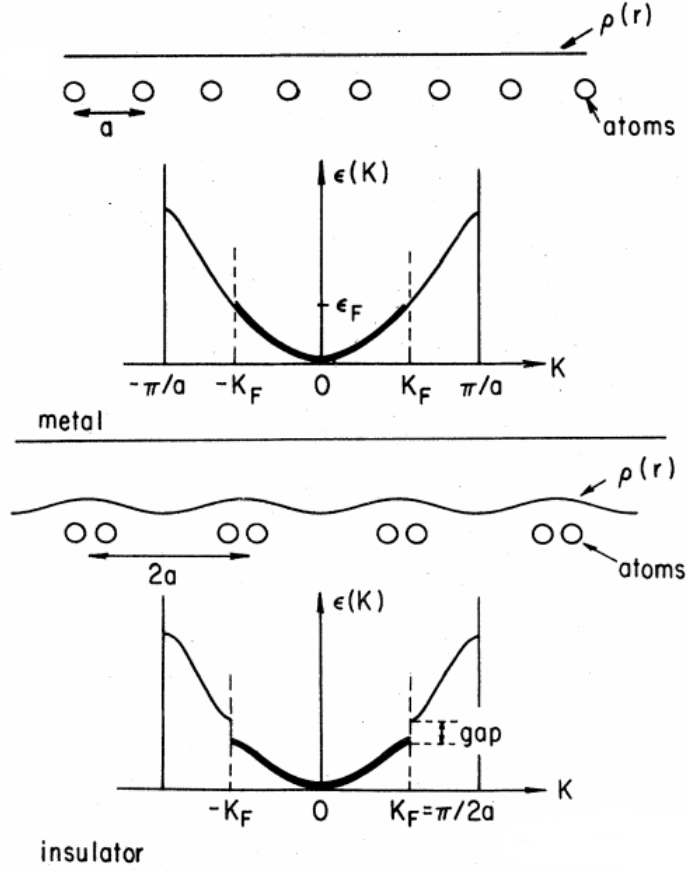


Figure 2.1: Peierls distortion in one dimensional metal with a half-filled band : undistorted metal and Peierls insulator in the upper part and lower part respectively [98].

in the vicinity of Fermi level. The distortion can be in axis and out of axis direction (zig-zag) as shown in Fig. 2.2 [97]. This phenomenon can be extended to the case of 2 and 3 dimensional materials. As we increase the temperature electrons will occupy higher energy states due to the thermal excitations. This will lead to the reduction of the band gap and degree of distortion. Eventually after certain threshold temperature so called Peierls temperature T_P the material will live through a second order transition and subsequently become a metal.

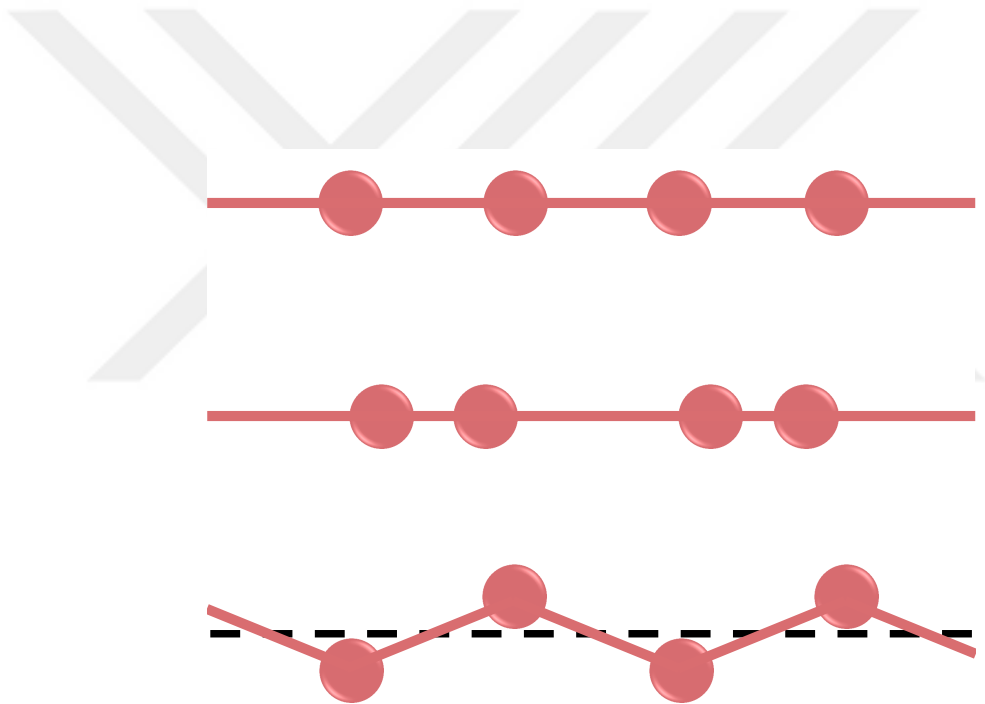


Figure 2.2: 1-dimensional metallic chain of atoms, in axis distortion and out of axis distortion from up to down respectively.

Chapter 3

New polymorphs of borophene

3.0.1 Structure and stability

As was mentioned previously boron crystals exhibit rich polymorphism and two dimensional domain is not an exception. Large number of flat boron polymorphs have been predicted using ab initio methods[39, 45] and 3 of them were realized experimentally using UHV MBE at high temperatures[32, 36]. Most of the structures are flat differing only in the density and arrangement of periodic holes within the sheets. However some of the boron sheets have non-planar *i.e* puckered structures such as buckled borophene[32], $Pmmn$ borophene and $Pmmm$ borophene[99].

Motivated by all these, we tried various geometries with the hope to find new possible structures of borophenes. Initially we tested a washboard configuration without a boron atom at the center of the hexagon (which is typical to two-dimensional black phosphorus (phosphorene)) as shown in Fig. 3.1 (a). However after multiple geometrical optimization steps it transformed into buckled triangular sheet. In the next step, we tested asymmetric washboard structure which is typical to monolayer antimonene as illustrated in Fig. 3.1 (b). Surprisingly, after structural optimization initial configuration transformed into unprecedented structure which is similar to washboard structure with an additional boron atom

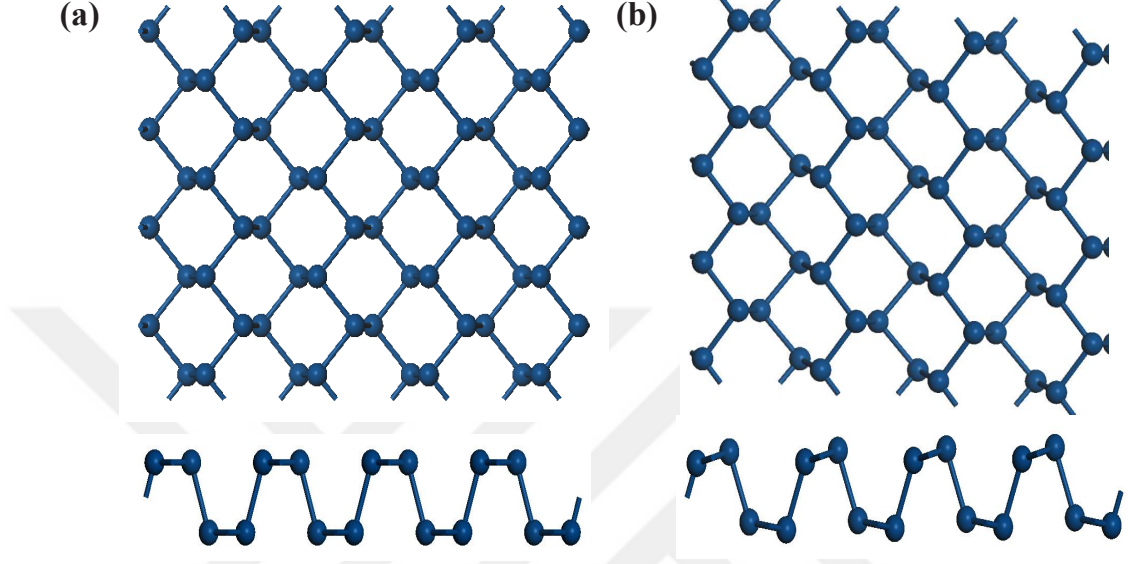


Figure 3.1: (a) Washboard structure which is typical to black phosphorus; (b) asymmetric washboard structure which is typical to antimonene.

at the center of the hexagon. We defined this structure as centered symmetric washboard (c-SW) because it resembles the washboard structure of phosphorene Fig. 3.2(a). The unit cell has lattice parameters of 1.62 Å and 5.13 Å in x and y directions respectively and it consists of 4 atoms. We used density functional perturbation theory (DFPT)[100, 101] based calculations and Phonopy software [102] to obtain phonon dispersion diagram and it was shown that this structure is stable at 0 K Fig. 3.2 (a). Moreover, to examine the thermal stability of the novel structure we performed *ab initio* molecular dynamics simulations (MD) using a larger 6x4 supercell. In these simulations, Nose thermostat[103] was used and Newton's equations were integrated through Verlet algorithm with a time step of 1 fs. Our simulations at temperatures ranging from 200-1000K showed that borophene can maintain its structural integrity throughout a 10-ps simulation but the c-SW transforms into new form of borophene with structural reconstruction. Briefly, distortions imposed by MD simulations allow to predict another structure which resembles asymmetric washboard structure monolayer antimonene Fig. 3.2(b). Structural reconstruction can be obtained when 2×1 unit cell is considered and we named this structure as reconstructed asymmetric

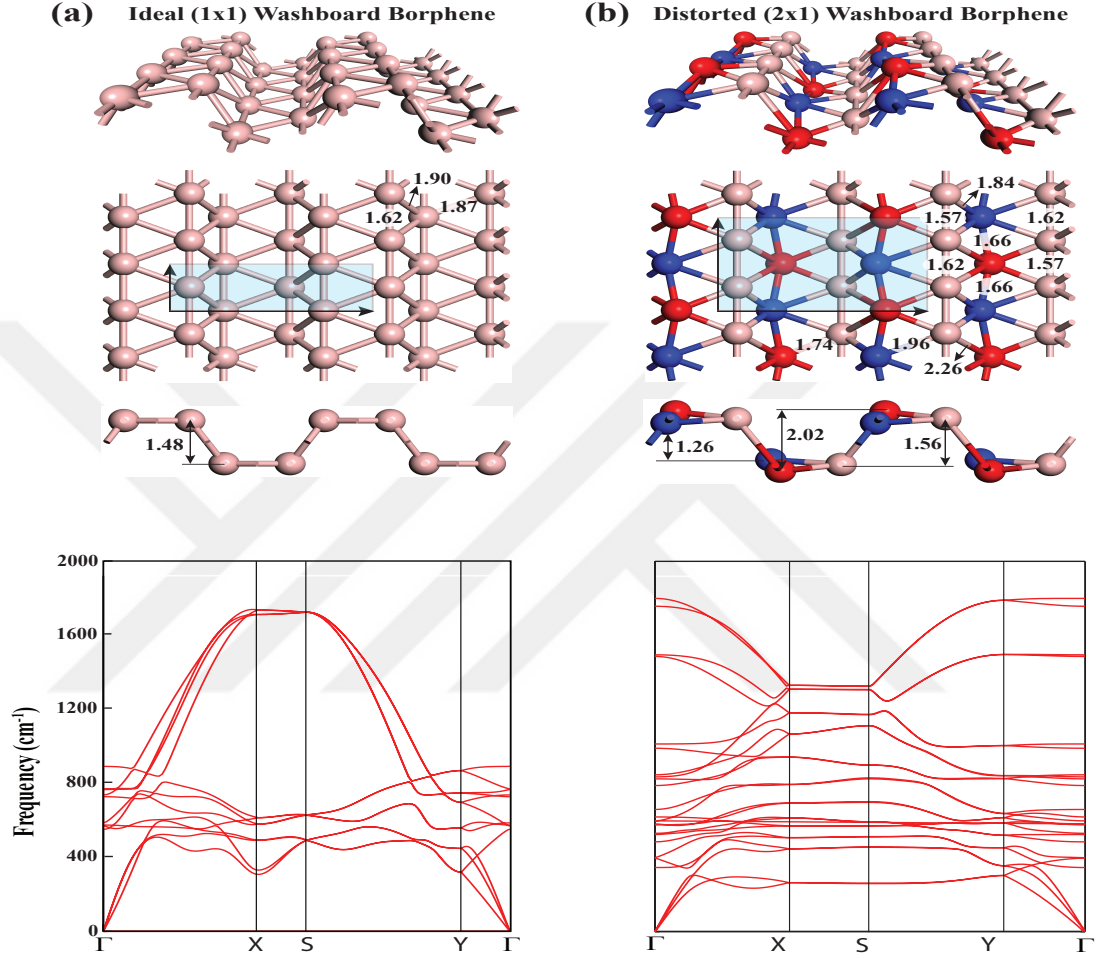


Figure 3.2: Perspective, top and side views of the structure and the phonon dispersion diagram of symmetric (a) and asymmetric (b) borophene.

wasboard (r-AW) phase of borophene. The unit cell has lattice parameters of $3.19 \text{ \AA}$ and $5.08 \text{ \AA}$ in x and y directions respectively and it contains 8 atoms per unit cell. Phonons dispersion diagram Fig. 3.2(b) shows that this structure is also stable at 0 K. Note that the lattice parameter of r-AW is two times larger than that of c-SW structure. For r-AW, we can see that along x direction we have two distinct chains of boron atoms. Both of the chains are distorted relative to c-SW. One of the chains (pink color) is distorted along the axis of the chain with the bond lengths of $1.57 \text{ \AA}$ and $1.62 \text{ \AA}$ and the other chain (red and blue color) has constant bond lengths equal to $1.66 \text{ \AA}$ but here the distortion is in the out

of axis direction. When total energies are compared, r-AW is energetically more favorable than c-SW.

3.0.2 Electronic properties

Next we analyzed the electronic structures as shown in the Fig. 3.3. The band diagram of c-SW borophene is metallic with Dirac-like point in the region between X and Γ and exactly at S high symmetry points. From the orbital projected DOS diagram we can see the high peak around the Fermi level originating from out of plane p_z orbital. Also note that there is wide band gap in the region between Γ and Y high symmetry points which indicates that this structure is highly anisotropic. Interestingly for the case of r-AW borophene we observe the band gap at the Fermi level indicating that this structure is a semiconductor with the band gap of 0.258 eV . So what is the reason behind such electronic transition? Why does highly conductive c-SW structure transforms in semiconducting r-AW one? The answer lies in Peierls instability of c-SW structure. Many polymorphs of borophene, including synthesized ones, are predicted to have a pronounced electron-phonon coupling which leads to superconductivity at low temperatures [49, 50] and c-SW polymorph should also have strong electron-phonon coupling due to high density of states around the Fermi level and low mass of B atoms. As was mentioned previously c-SW structure is highly anisotropic in terms of electronic structure. These reasons make c-SW borophene a perfect playground for Peierls transition. Indeed the fact that highly conductive c-SW structure transforms into r-AW structure which consists of 2 chain of B atoms with alternating bonds makes it clear that we are dealing with the perfect example of Peierls transition in a 2D system.

3.0.3 Mechanical properties

In the next step we applied strain to the r-AW structure along the axis of chains of atoms (x direction) and Fig. 3.4(b) shows how electronic bands diagram changes

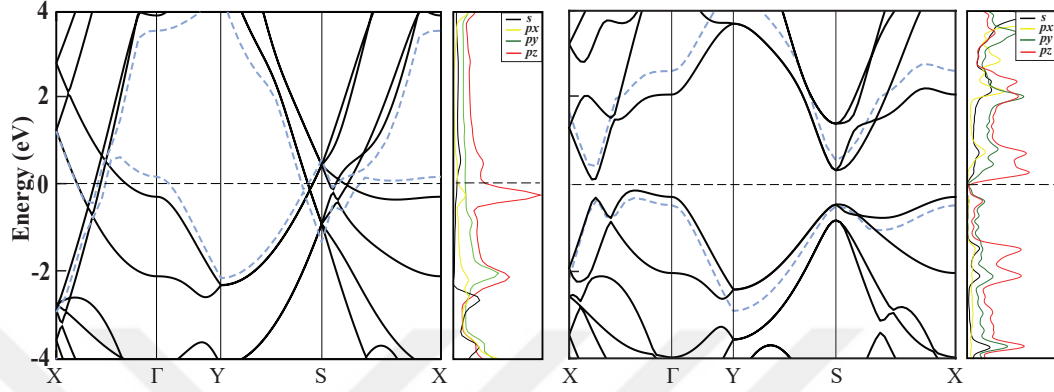


Figure 3.3: Electronic band and orbital projected density of states diagrams of symmetric (a) and asymmetric washboard (b) borophene. Blue dashed lines represent valence and conduction bands calculated using HSE06 hybrid functional.

upon application of strain. We observed that the c-AW borophene the band gap narrows down with tensile strain and at 2% strain valence and conduction bands start to cross the Fermi level (PBE functional) which indicates that the system becomes metallic. At 5% strain r-AW borophene structurally transforms into SW borophene. Another very interesting point about new phases is that, while semiconducting phase exhibits positive Poisson's ratio metallic phase has the negative one. Other anisotropic materials such as phosphorene and buckled triangular borophene also exhibit negative Poisson's ratio [32, 104, 105]. Borophene structures are predicted to exhibit profound mechanical properties such as high Young's modulus, flexibility and negative Poisson's ratio which makes them promising in the area of stretchable electronic devices [106]. The structures that we predicted confirm this behavior of boron based nanosheets. Further investigation of the mechanical and electronic properties of borophenes is fundamentally important.

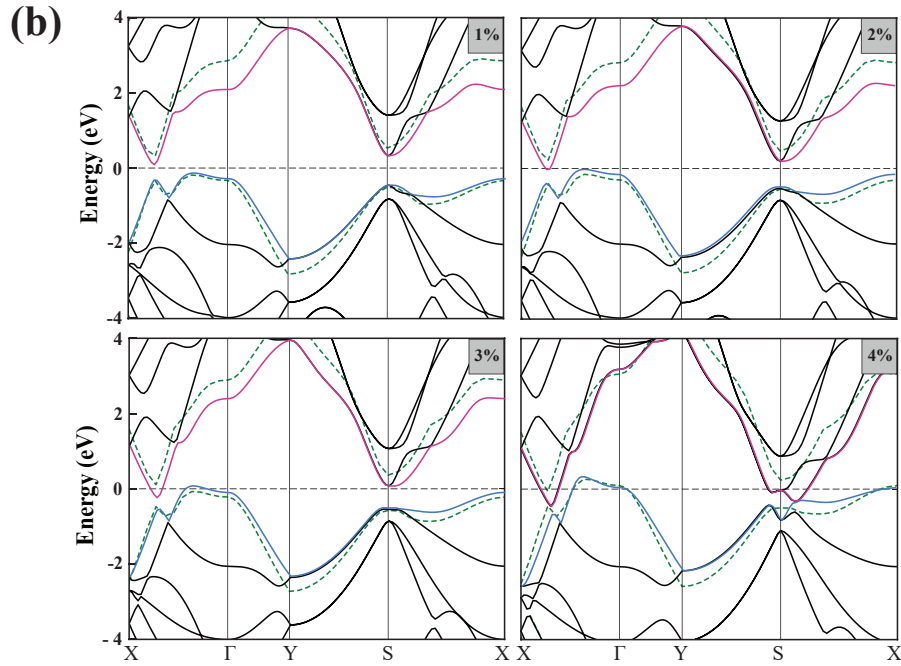
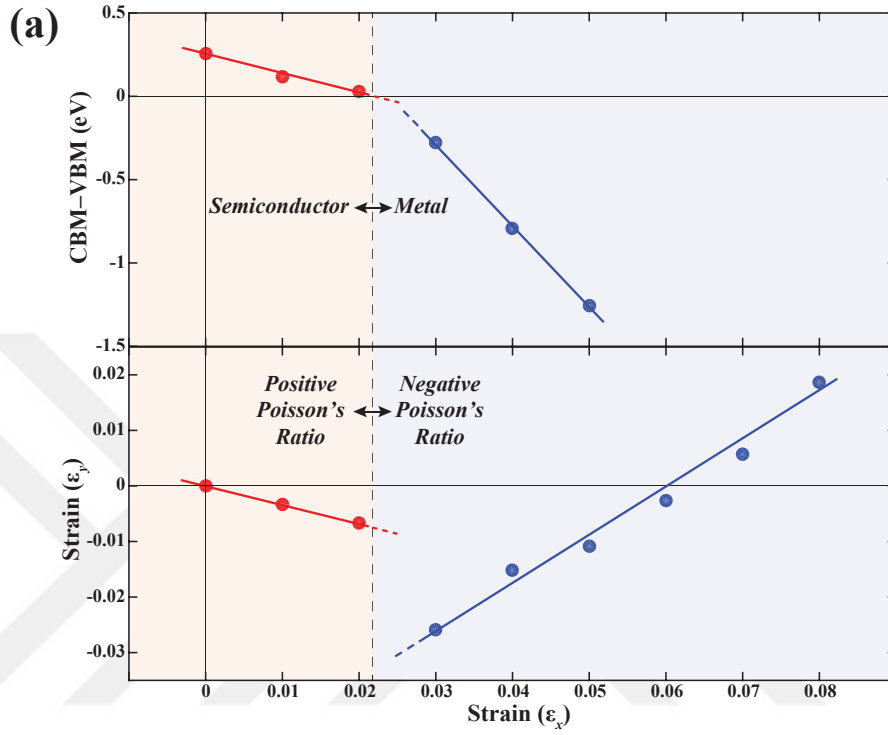


Figure 3.4: (a) Difference between conduction band minimum (CBM) and valence band maximum (VBM) vs strain in x direction ϵ_x and strain in y direction ϵ_y vs strain in x direction ϵ_x . (b) Electronic band structure of asymmetric washboard borophene under 1% , 2%, 3% and 4 % strains. Dashed lines represent CBM and VBM calculated by HSE06 hybrid functional

Chapter 4

The Interaction of Halogen atoms and molecules with buckled borophene

4.0.1 Structure and energetics

The adsorption of halogen atoms can substantially modify the physical and chemical properties of borophene and enhance the stability of borophene by accepting the electrons from antibonding states [32]. Revealing the process of doping is also essential for plausible halogenated derivatives of borophene. To study the adsorption of single halogen atom (X: F, Cl, Br, I), we start with structural optimization of monolayer borophene. The optimized lattice constants of pristine borophene are calculated as $\mathbf{a}=1.62$ Å and $\mathbf{b}=2.86$ Å with a buckling of 0.90 Å which are in agreement with previous studies [32, 107]. The coupling between X atoms are minimized by using 7×4 borophene supercell (with lattice parameters of 11.30 Å and 11.45 Å) which is tested to be sufficiently long enough in both directions. This system, as shown in Fig. 4.1, contains 56 B and 1 X atoms which is equivalent to the halogen concentration of 1.75%.

Four possible sites are considered for adsorption as shown in Fig. 4.1: top of

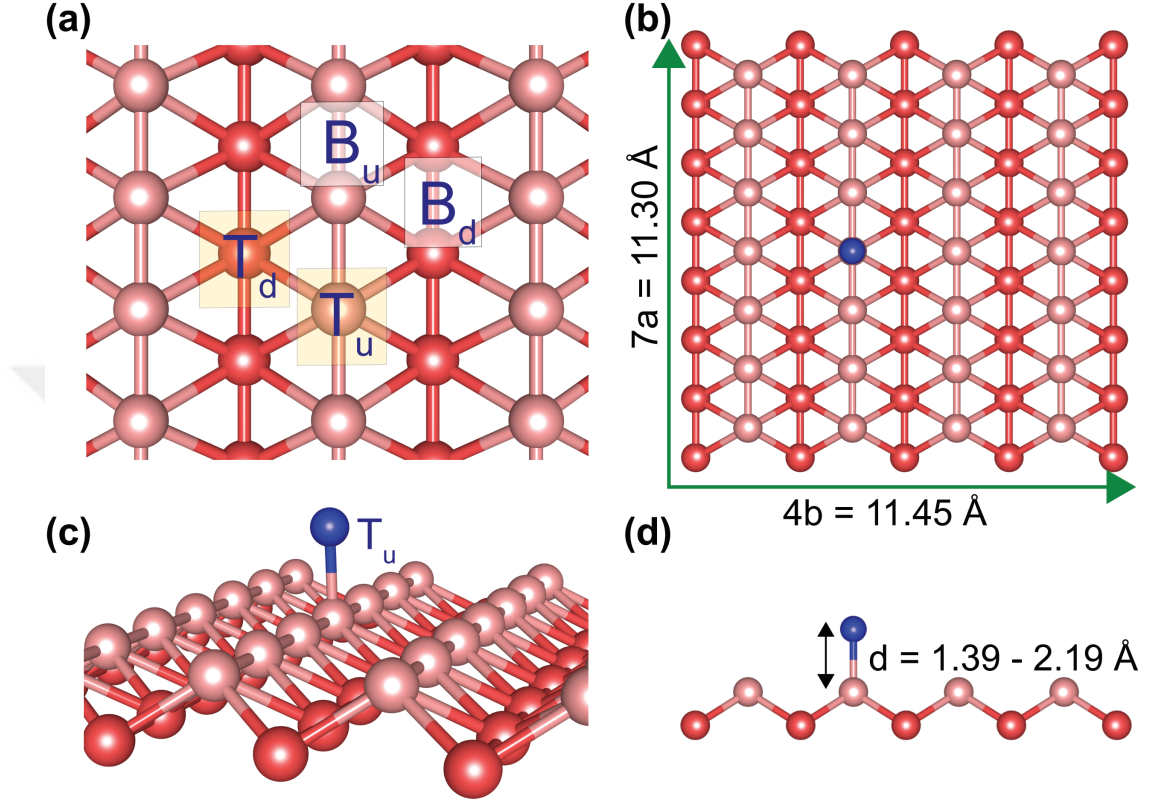


Figure 4.1: (a) The possible adsorption sites on borophene sheet: top of B atom on the upper (T_u) or lower layer (T_d), above the middle of successive B atoms on the upper (B_u) or lower layer (B_d). (b) Top (c) Perspective and (d) Side view of the 7×4 supercell with single adatom (X:F, Cl, Br, I) on T_u site. Boron atom on the upper (lower) layer and halogen atoms are shown by light (dark) red and blue spheres, respectively.

B atom on the upper (T_u) or lower layer (T_d), above the bridge of successive B atoms on the upper (B_u) or lower layer (B_d). Our results indicate that only T_u and B_d are stable adsorption sites and adatoms on T_d and B_u slide to T_u which is the ground state configuration for all X atoms. Top site is also favored for halogen atoms adsorbed on monolayers of Group IV elements [62, 66, 71, 72, 73]. Adsorption energy (E_b), formation energy (E_f), dissociation energy of a halogen molecule (E_{dis}), bonding distance between B and X atoms (d_{B-X}), and the amount of charge transferred to X atoms (ρ_X) for the ground state configuration (T_u site) is summarized in Table 4.1. E_b for the other stable site, B_d is also given in parenthesis for comparison.

Atom	E_b [eV]	E_f [eV]	E_{dis} [eV]	d_{B-X} [Å]	$\Delta\chi$	ρ_X [e]
F	5.03 (4.08)	3.87	-1.15	1.36	1.94	-0.79
Cl	3.23 (2.67)	1.81	-1.42	1.79	1.12	-0.63
Br	2.64 (2.17)	1.41	-1.23	1.97	0.92	-0.48
I	2.09 (1.76)	0.98	-1.12	2.19	0.66	-0.14

Table 4.1: Adsorption energy (E_b), formation energy (E_f), dissociation of a halogen molecule (E_{dis}), bonding distance between B and X atoms (d_{B-X}), the electronegativity difference between B and X atom ($\Delta\chi$) and the amount of charge transferred to X atoms (ρ_X) are given for the ground state configuration (T_u site). E_b for other stable site, B_d , is given in parenthesis. All energies are given per atom.

Upon adsorption, all X atoms slightly distort the pristine borophene by attracting the underlying B atom at T_u . The amount of distortion decreases from F to I atom. The calculated E_b is high for all X atoms indicating a strong chemical binding. At B_d , each X atom attracts two B atoms at T_u and makes bonds with both of them. As will be discussed later in this section, this configuration is fragile and can only be stable at low temperatures. The highest E_b is obtained for F which is 5.03 eV and decreases gradually to 2.09 eV down the group. In addition, all calculated formation energies are positive indicating that the adsorption of halogen atoms on borophene is an exothermic process. The calculated d_{B-X} is only slightly larger than those reported for boron trihalides, thus the bonding characters are expected to be analogous. Not suprisingly, d_{B-X} shortens with increasing E_b indicating a stronger bond. The variations of E_b and d_{B-X} with the type of X atom are shown in Fig. 4.2. The strength of binding can also be linked to the amount of charge transfer from borophene to X atoms. The Bader analyses demonstrate that while F accepts -0.79 $|e|$ (negative value indicates that charge is accepted by X atoms), it is only -0.14 $|e|$ for I. ρ_X decreases down the group following the same trend of $\Delta\chi$ as illustrated in Fig. 4.2.

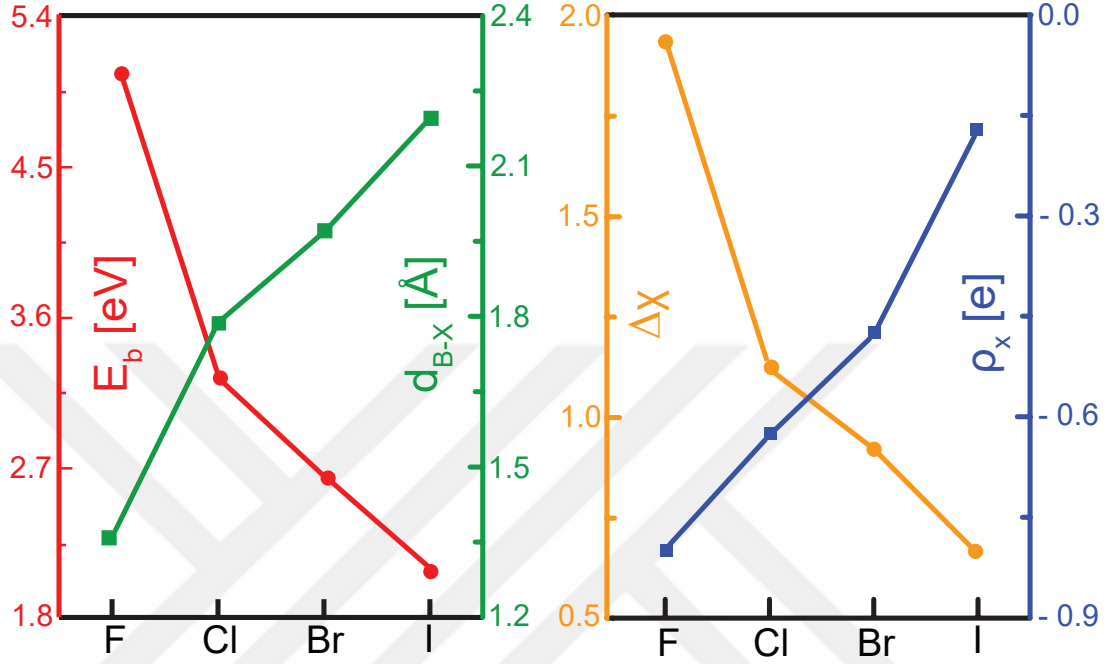


Figure 4.2: The variation of (a) E_b (red line), d_{B-X} (green line), and (b) $\Delta\chi$ (orange line), ρ_X (blue line) with type of X atom.

4.0.2 Diffusion of adatoms

The calculated E_b values are significantly higher than those which are obtained for interaction of X atoms with Group IV sheets. For instance, E_b is reported as 2.71 eV[62], 1.13 eV[66], and 0.86[68] eV for F, Cl, and I adsorption on graphene, respectively. Interestingly, other widely used adatoms such as H, Li and O also strongly bound to borophene with E_b of 2.99 eV[108], 2.84 eV[108] and 4.55 eV,[107] respectively. These results also indicate that borophene has a very reactive surface. The lateral diffusion of X atoms on borophene surface from T_u to the first nearest T_u ($T_u \rightarrow T_u$) and then to the next nearest B_d ($T_u \rightarrow B_d$) is calculated by using NEB method.[95, 96] The variation of total energy along this path together with relevant energy barriers for Cl atom is shown in Fig. 4.3(a) as an example. Two significant barriers are noticed: along $T_u \rightarrow T_u$ (Q_1) and along $T_u \rightarrow B_d$ (Q_2). Both Q_1 and Q_2 are high and this lowers the possibility of migration of X atoms on the surface. Calculated diffusion barriers are substantially higher than those are obtained for graphene where migration occurs

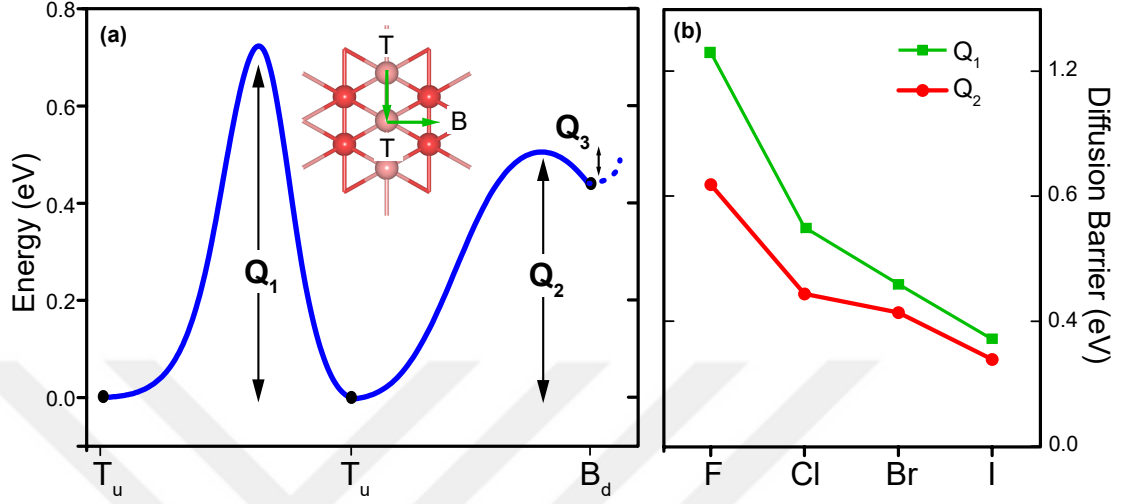


Figure 4.3: (a) The variation of total energy along the diffusion path together with relevant energy barriers for Cl atom. Zero of energy is set to the ground state energy at T_u . The diffusion path is shown as an inset. (b) The variation of diffusion barriers, Q_1 (from T_u to T_u) and Q_2 (from T_u to B_d) with the type of halogen atoms.

with almost no barrier.[66] On the other hand, the barrier is very low along $B_d \rightarrow T_u$ for all cases ($Q_3 < 60$ meV) indicating that B_d site is stable only at low temperatures, and X atoms remain bound only to T_u at ambient conditions. Q_1 and Q_2 decrease down in the group as illustrated in Fig. 4.3(b) and the highest energy barrier is obtained for F.

4.0.3 Bonding mechanism

Next, we analyze the nature of bonding between X atoms and borophene. While B atoms have three valence electrons, each of them has six nearest neighbors in buckled triangular borophene. Accordingly, unlike 2D Group IV systems, some of the in-plane sp^2 antibonding states are occupied [109] and borophene has tendency to donate electrons. Taking the high χ of halogens into account, charge transfer from borophene to X atoms upon adsorption as given in Table 4.1 is expected. ρ_X is the highest for the case of F atom. The charge difference analyses indicate that the transferred charge is not only accumulated on F atom

but also between F-B bond. The charge is depleted from the nearby B atoms as shown in Fig. 4.4(a). As $\Delta\chi$ between F and B is high ($\Delta\chi \sim 2$), the bonding has mainly an ionic character. Interestingly, a recent study reported that adsorbed H atom also extracts charge from borophene and amount is calculated as $-0.72|e|$, which is comparable to the case of F atom[110, 108]. The charge profile is similar for other halogen atoms as well. As discussed above, ρ_X is correlated with $\Delta\chi$ (Fig. 4.2(b)) and thus decreases down the group which is also noticeable from the charge difference analysis shown in Fig. 4.4(b-d). Different from F case, charge is accumulated more on the B-X bond for other halogen atoms and bonding has more covalent character.

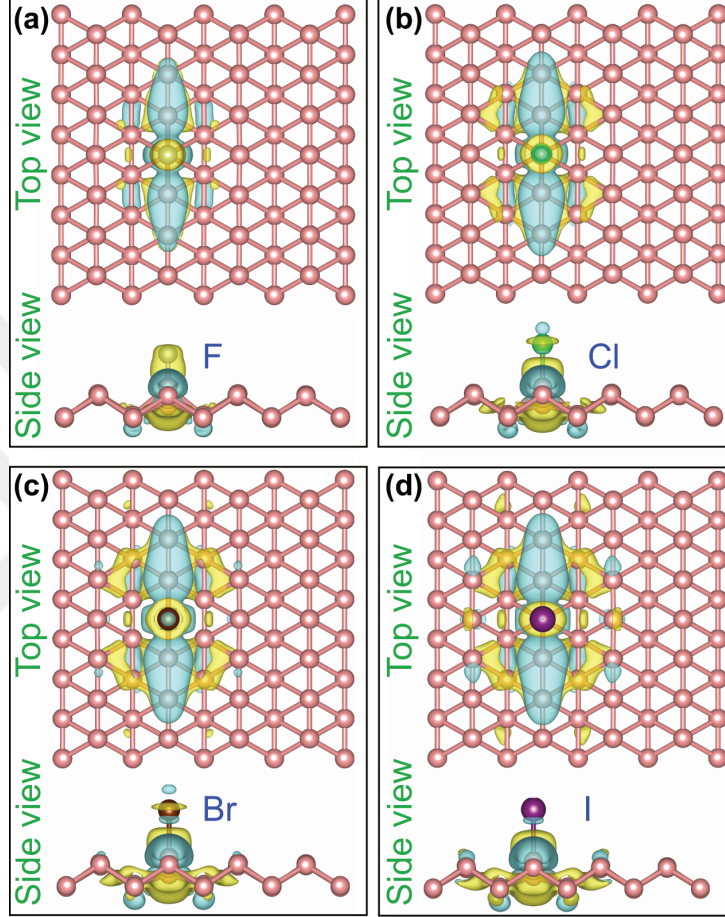


Figure 4.4: The charge density difference profiles of (a) F, (b) Cl, (c) Br, and (d) I doped borophene for 7×4 supercell. Yellow and blue color represent charge accumulation and depletion, respectively.

In general, in-plane bonds resulting from sp^2 hybridization are stronger than out-of-plane bonds. This makes buckled triangular borophene less stable than planar α - and β -borophene polymorphs where two- and three-center bondings are balanced. Therefore, halogen atoms which act as electron acceptors, can extract excess electrons occupying antibonding states which enhances stability of buckled borophene.

Following this discussion, we also analyzed the projected density of states (PDOS) to reveal the orbital contributions to bonding. PDOS of in-plane and

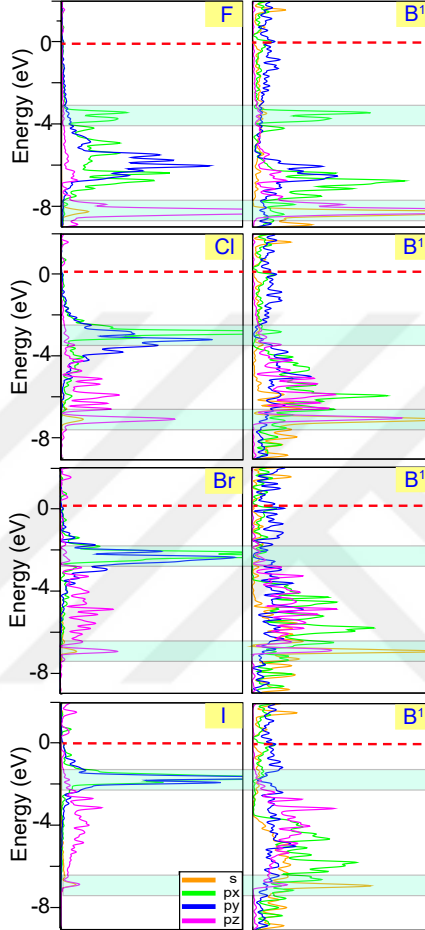


Figure 4.5: Orbital decomposed projected density of states (PDOS) of F, Cl, Br, and I and the first nearest B atom at T_u site (B^1). Main peaks are highlighted with light green.

out-of-plane states for X and B atom on T_u (B^1) are shown in Fig. 4.5 and the contributions from the second and the third nearest B atoms (B^2 and B^3) are given in Fig. 4.6. Our results indicate that while Cl, Br, and I have similar bonding character, F differs from them. Upon adsorption, bonding states of F and B at T_u are occupied and bonding is mainly formed from hybridization of p_z orbital of F, and s - p_z orbitals of B^1 . This state is at -8.2 eV where Fermi level (E_F) is set at 0 eV. Another bonding state (π bonding) can be noticed at -3.5 eV upon hybridization of p_x orbitals and not only B^1 but B^2 and B^3 atoms contribute as well. For other X atoms (Br, Cl, and I), s - p_z hybridized state is localized at

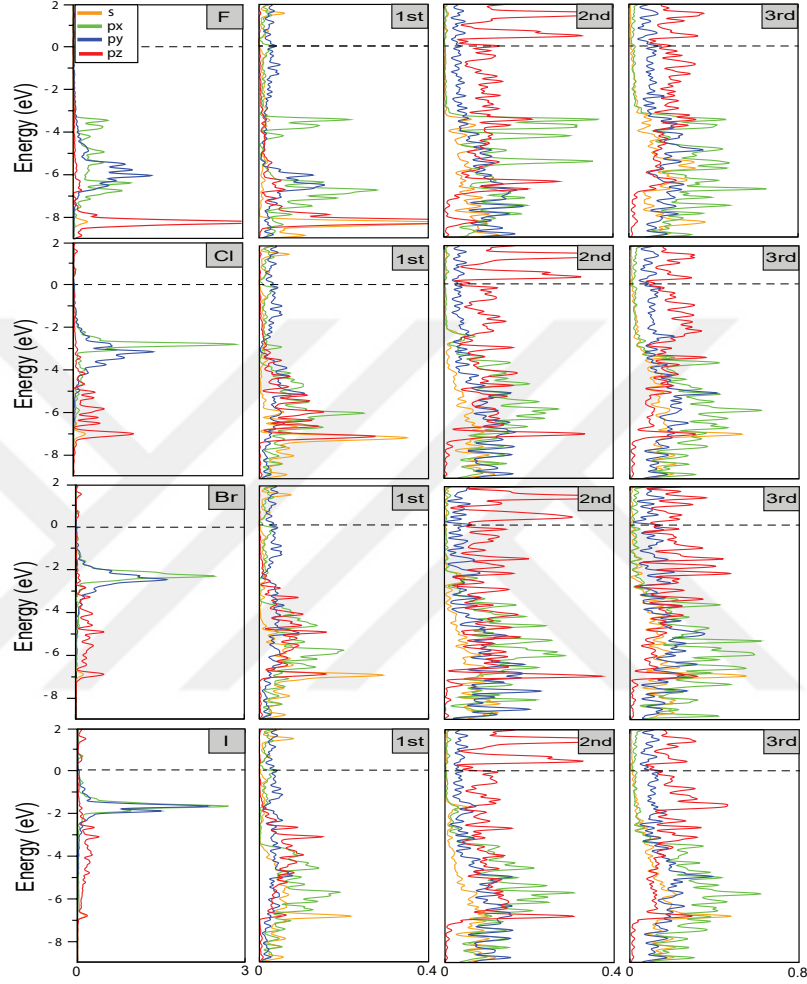


Figure 4.6: Orbital decomposed projected density of states (PDOS) of F, Cl, Br, and I and the first, second and third nearest B atoms.

~ -7 eV. While the contribution from p_z orbital of X and B^1 reduces down in the group, it increases for B^2 and B^3 . Other bonding state due to hybridization of p_x orbitals weakens progressively with size and almost diminishes for I. This level is -1.9 eV for I and deepens moving up to F. The small atomic size and high χ of fluorine mainly account for the differences between F and other halogen atoms. Lastly, we analyzed the electronic structure of X-doped systems by calculating the band structures. The pristine borophene is metallic with bands crossing E_F only along the directions parallel to uncorrugated (armchair) direction. This results in an anisotropy and the electrical conductivity is confined only along this direction.

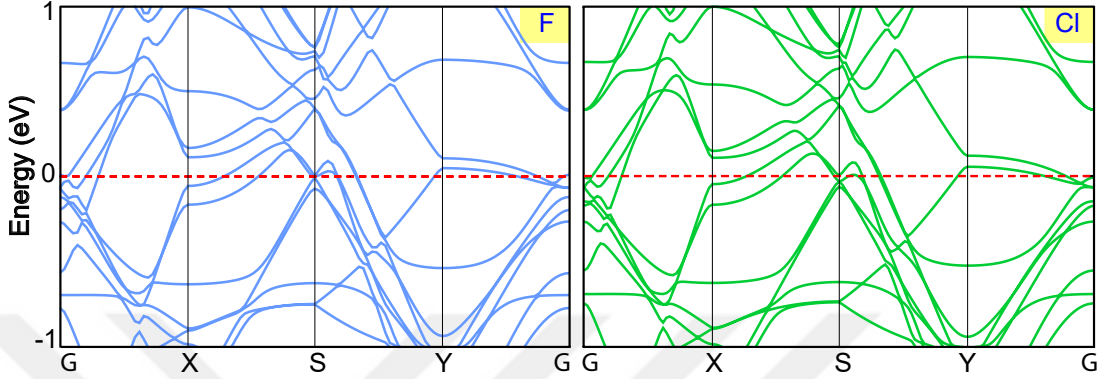


Figure 4.7: The band structures of F- (left) and Cl-doped (right) borophene along high-symmetry directions. The Fermi level is set to zero and is shown by a dashed red line.

The band structures of X-doped systems as shown in Fig. 4.7 indicate that X atoms not only generate deep localized states (Fig. 4.5), but modify the electronic structure. Upon adsorption, bands cross the E_F along all the directions and it makes the system more isotropic. Furthermore, an enhancement in electrical conductivity can be expected due to the increased number bands crossing the E_F . This modification is related to structural distortion and change in the charge distribution (Fig. 4.4). Another interesting feature on the band profile is the band crossing at S -symmetry point for F-doped system. Similar crossing is also obtained for other X atoms but slightly below E_F . These results indicate that the electronic properties of borophene can be modified upon passivation with halogen atoms, suggesting a new material similar to hydrogenated borophene [110] or halogenated Group IV systems [111, 67, 66].

4.0.4 Molecular adsorption

Due to their high reactivity, halogens naturally occur in molecular form (X_2) with relatively low intermolecular bond energy when compared to other diatomic molecules (e.g. H_2 , O_2 , N_2) or their compounds with other atoms (e.g. HX , CX_4). Interaction of X_2 molecules with Group IV systems has been studied extensively [112, 68, 113] and they are considered as molecular impurities. They

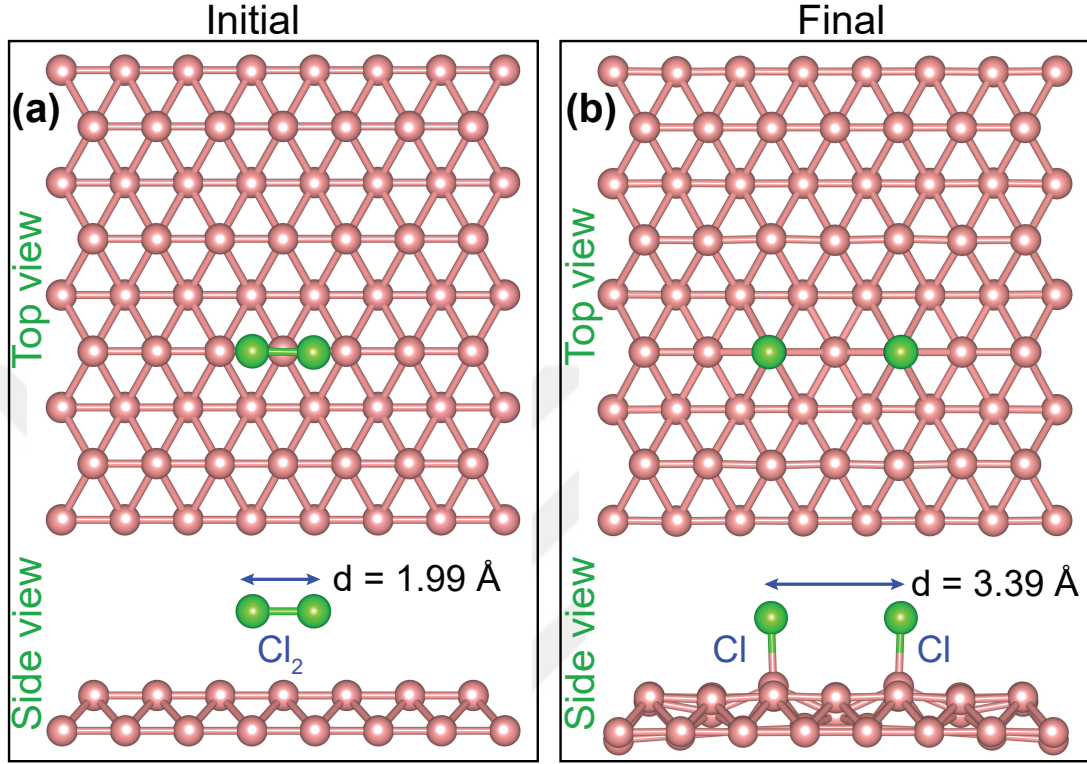


Figure 4.8: (a) Initial and (b) final configurations of top and side view of Cl_2 adsorption on borophene sheet. All halogen molecules dissociate into separate atoms as in the case of Cl_2 .

generally interact weakly with 2D sheets and are physisorbed in molecular form. In a similar manner, together with single atom adsorption, we studied the interaction of X_2 molecules with borophene. We tested various sites with different parallel and vertical orientations. Interestingly, for all cases X_2 dissociates spontaneously without an activation barrier and is atomically adsorbed on the nearest T_u sites. The dissociation energy (E_{dis}) for X_2 molecules in vacuum is given in Table 4.1. The parallel adsorption case for Cl_2 , which has the highest molecular bonding energy among halogens, is shown in Fig. 4.8 as prototype. Other configurations are shown in Fig. 4.9 X_2 also dissociates for perpendicular adsorption but this time while one of X binds to B atom at T_u site, the other one ascends. Dissociation can be explained by the charge transfer from B to X atoms which weakens the X-X interaction. Spontaneous dissociation of X_2 molecule suggests fast adsorption rates [114] and also indicates the high reactivity of borophene sheet.

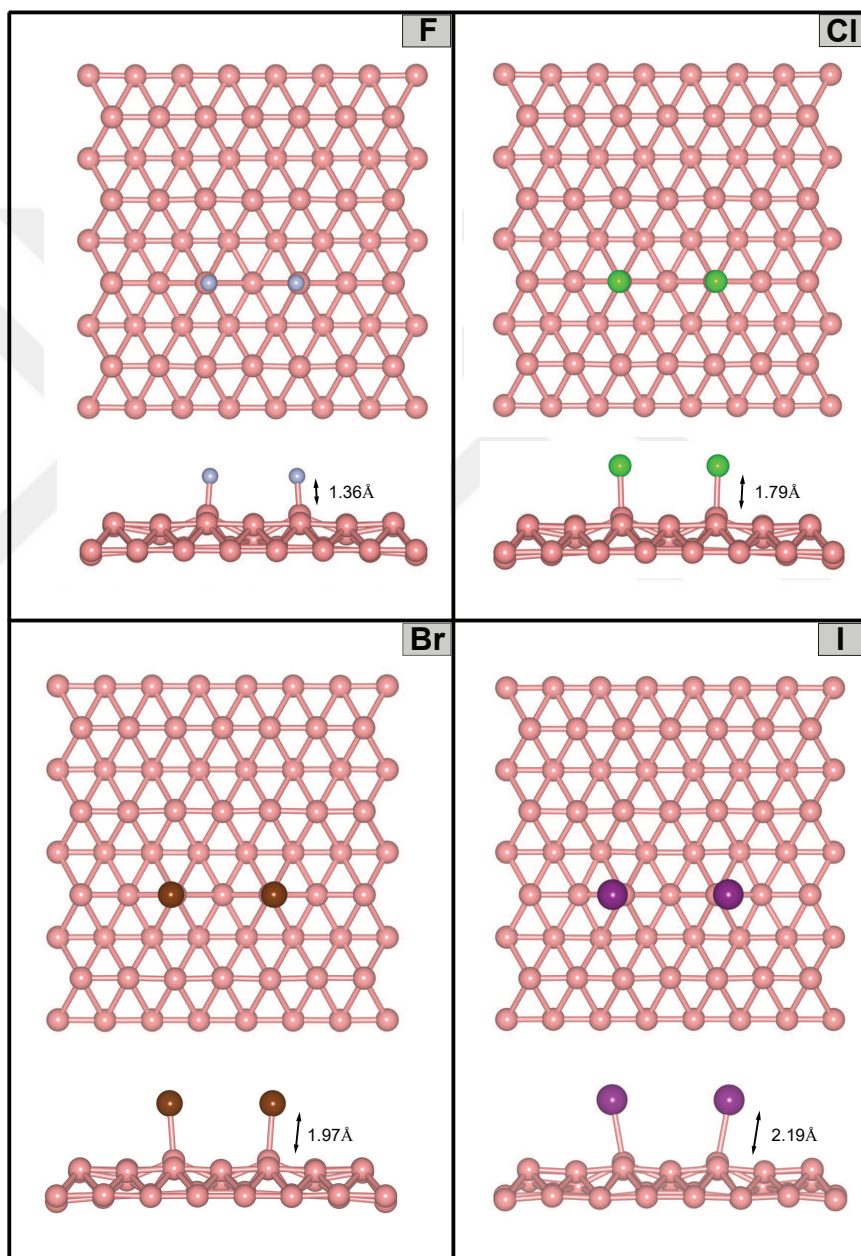


Figure 4.9: Final configurations of top and side view of X_2 adsorption on borophene sheet. All halogen molecules dissociate into separate atoms.

Chapter 5

Conclusion

In this thesis we reported the discovery of two novel phases of borophene namely centered symmetric washboard c-SW) and reconstructed asymmetric washboard (r-AW) structures using *ab initio* methods based on DFT. These polymorphs possess unprecedented crystal structures resembling the monolayer phosphorene and antimonene. Phonon dispersion diagrams obtained by density functional perturbation theory based methods showed that these structures are dynamically stable. r-AW structure can be viewed as 2×1 reconstructed c-SW structure with the in plane and out of plane distortions within the chains of boron atoms. The reason for distortions lies behind the Peierls instability of c-SW borophene which results in structural reconstruction. Due to structural phase transition we observed concomitant metal to semiconductor transition. Interestingly despite the structural similarity of these structures they exhibit different mechanical properties in the sense that while r-AW has a positive Poisson's ratio c-SW structure has positive one. Molecular dynamics simulations showed that c-SW structure is stable at very low temperatures and at finite temperatures it transforms into r-AW phase. These results prove that further fundamental understanding of boron monolayer sheets is required and device application of borophenes has a great promise due to the peculiar properties these materials.

In addition to that we systematically studied the interaction of halogen atoms

with buckled borophene. We tested all possible adsorption sites and determined that the ground state configuration is the top of the B atom in the upper layer in parallel with the results obtained for monolayers of group IV elements. Upon adsorption all halogen atoms extract a substantial amount of charge from the boron sheet. The amount of charge transfer decreases from F to I atoms, which is correlated with the change in the electronegativity that progressively decreases with size. The charge transfer also determines the strength of binding and halogen atoms are strongly bound to borophene. The obtained energy barriers along the diffusion paths are notably high indicating low possibility of migration of adsorbed atoms. The nature of s bonding is mainly determined by the hybridization of the p_z orbital of the X atom and the $s-p_z$ orbital of the first nearest neighbor B atom. This bonding character is more significant for the F atom case which in general differs from other halogens. Doping also modifies the electronic structure of borophene. However, borophene remains metallic (differing from the pristine case) and bands cross the Fermi level in all directions, mainly altering the anisotropic nature of electrical conductivity.

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