First-principles study on the atomic structure of two-dimensional molybdenum boride

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Abstract

In recent years two-dimensional (2D) materials have attracted extensive research due to their excellent physical properties in thermoelectricity and superconductivity, etc. This interest led to both a new wave of research on known 2D materials, such as transition metal nitrides (MXene), and the discovery of many new 2D materials. Recently, the 2D metal borides Mo\textsubscript{4}/B\textsubscript{2−x} with ordered metal vacancies were successfully synthesized. However, variable atomic structures were experimentally observed in the specimen, suggesting that more than one structure exists in this 2D material. Therefore, in this work, the stabilities of molybdenum boride with different Mo content are examined employing first-principles calculation based on the density functional theory. The binding energies of different molybdenum boride models are calculated and analyzed, and the effect of the Mo content on their stability was investigated. The chemical bonding properties are also analyzed via electron localization functions, which further answer why the experimentally synthesized molybdenum borides would have different atomic structures.

1. Introduction

The pioneering two-dimensional (2D) material, graphene, was firstly isolated from graphite in 2004 [1]. This brand-new material has fascinating structure, one-atom-thick monolayer honeycomb allotrope of carbon, which contribute to its excellent performance in various fields. Its superior thermal, mechanical, optical and electrical properties quickly attracted tremendous researchers to investigate its functionalized application [1–5]. Furthermore, many methods have been devised for synthesizing graphene, such as solvothermal, solution based, ultra-high vacuum (UHV) surface epitaxial approaches and topotactic [6–8]. In the wake of the great success of graphene, the development and application of new two-dimensional materials with unique properties dominated by its structure has become a new trend in research [9–12]. Novel 2D materials, honeycomb monolayer h-BN, silicagraphene, metal dichalcogenides (e.g., Mo\textsubscript{2}S, WS\textsubscript{2} etc), boron nitride and MXene have been fabricated and quickly became the research hotspots [9, 13–17]. The MXene, in which transition metals are involved, has greatly enriched the family of two-dimensional materials. Additionally, as the research progresses, the techniques for exfoliating 2D materials from the solid phase are also improved: liquid phase exfoliation, electrochemical exfoliation, chemical vapor deposition (CVD), etc [2]. Traditionally, the two-dimensional material MXene is obtained by selective etching the A element from the MAX phase of ternary transition metal carbides, carbon nitrides or nitrides with the general formula M\textsubscript{n−1}AX\textsubscript{n} (n = 1, 2, 3) [16]. For example, Naguib et al [18] used hydrofluoric (HF) acid to extract the Al layer from Ti\textsubscript{3}AlC\textsubscript{2}, and followed by ultra-sonication treatment in methanol to obtain single layer, double layers, and multilayers Ti\textsubscript{3}C\textsubscript{2}.

Conventional MXene materials are mainly focused on transition metal carbides and nitrides [19]. In last year 2D molybdenum boride, Mo\textsubscript{4}/B\textsubscript{2−x}, has been successfully synthesized in an experimental environment [20], marking a further expansion of the family of 2D materials. Compared with MAX phase, replacing carbon with...
boron which has similar chemical properties, ternary laminated boride phase is named as MAB. In-plane chemically ordered MAB phase quaternaries, coined i-MAB, could enable the synthesis of 2D molybdenum borides with ordered metal vacancies, which may hold promise in energy storage and catalysis. In the work of Zhou et al. [20], the scanning transmission electron microscopy (STEM) images were used to speculate and conceive an ideal configuration of 2D Mo$_{4/3}$B$_{2-x}$ and a rough simulation of this ideal structure have also been done. The single-layer Mo$_{4/3}$B$_{2-x}$ obtained by selective etching from i-MAB phase are subject to ordered metal vacancies. However, the experimentally observed STEM image of Mo$_{4/3}$B$_{2-x}$ shown more than one atomic structure and an inhomogeneous density of metal vacancies in this material due to stripping and readorption of Mo atoms. Therefore, the atomic structure stability and interatomic bonding strength of 2D molybdenum borides need to be further investigated.

In the present work, we have investigated the relative stabilities of twelve molybdenum boride models using first-principles calculation based on the density functional theory. The binding energies of these molybdenum boride structures were calculated and the influence of the Mo content to their stabilities was analyzed. The STEM images of several most stable structures were simulated and compared to the experimental observations. In addition, we have calculated the electron localization function of the molybdenum boride system and analyzed the origins for the experimentally observed different structures of Mo$_{4/3}$B$_{2-x}$ from interatomic bond strength and structure stability, which has significant implications for the synthesis and application of 2D molybdenum borides.

2. Methodology

Density Functional Theory (DFT) reveals that the electron density of a many-electron system can solely determine the properties of this system [21, 22], which allows the properties of materials to be investigated directly from the atomic scale where the electron wave function can be solved for. Therefore, the electronic structure properties of system, e.g. bonding analysis [23], charge transfer [24], can be revealed by the first-principles based on density functional theory. Moreover, the high precision first-principles calculation can accurately predict the structural stability and phase stability of materials, which has been shown in previous work [25–27]. Based on this reliable theoretical simulation framework, the first-principles method was employed to investigate the stability of two-dimensional molybdenum boride with different atomic arrangement in this work.

The 2 × 2 × 2 supercell models were constructed for first-principles calculations in order to take into account the atomic structure variety with composition. With reference to the 2D Mo$_{4/3}$B$_{2-x}$ that has been synthesized in experimentally and its 3D i-MAB phase, we constructed twelve molybdenum boride structure models by considering different Mo content. This includes three and six models with the top and bottom metal atoms symmetrically and asymmetrically arranged respectively about the boronene in xy plane, as well as three models in which only one Mo-layer is considered. The vacuum layer of all 2D molybdenum boride structures was set to be 25 Å to avoid spurious interactions between the neighboring images along the z direction.

All first-principle calculations in this work were performed by using the Vienna ab initio simulation package (VASP) [28], which based on high-precision plane-wave basis sets. The projector-augmented wave (PAW) was selected to describe the electron-ion interactions [29]. The generalized gradient approximation (GGA) as parametrized by Perdew–Burke–Ernzerhof (PBE) [30] was used to treat the electron exchange and correlation effects. The energy cutoff for the plane-wave basis set expansion was set to 480 eV. The Monkhorst-Pack scheme [31] was used for k-points sampling in the Brillouin zone. All calculations of structure optimization were performed using k-grids of 8 × 8 × 1 points. To obtain reliable optimized structures, the maximum residual force on each atom is less than 0.01 eV Å with respect to ionic relaxation and the electronic self-convergence criterion was set to 1.0 × 10$^{-6}$ eV for all structures. The binding energy is the energy required to form a solid from the separated neutral atoms in their ground electronic state [32], which is the simplest and most intuitive means of evaluating the stability of different structures of the system and can effectively characterize the overall stability of the system [33].

For a system of N atoms, which contains $n_A$ A atoms and $n_B$ B atoms, the binding energy was calculated as follows:

$$E_b = - (E_{tot}^{AB} - n_A E_{atom}^A - n_B E_{atom}^B) / N$$

where $E_{tot}^{AB}$ is the total energy of the system, $E_{atom}^A$ and $E_{atom}^B$ are the isolated atomic energies of atom type A and type B respectively. In this work, for the 2D molybdenum boride, the atoms A and B in the binding energy equation correspond to the Mo and B atoms, respectively. Cells with a side length of 20 Å, which contain only one Mo or B atom in the central position, were used for Mo and B isolated atomic energy calculations. The k-grids of 1 × 1 × 1 Gamma point were used, while ensuring that the total energy convergence accuracy is the same as that set for the 2D molybdenum boride. In addition, we employed the QSTEM software package to
simulate STEM images of the possible molybdenum boride structures and compare them with experimental observations. Visualization of Electron Localization Function (ELF) was done with the VESTA code.

3. Results and discussion

Mo$_{4/3}$B$_{2-x}$ is a new two-dimensional metal boride with the metal vacancies, which produced by selective etching of aluminum and yttrium or scandium atoms from 3D in-plane chemically ordered (Mo$_{2/3}$Y$_{1/3}$)$_2$AlB$_2$ and (Mo$_{2/3}$Sc$_{1/3}$)$_2$AlB$_2$ in aqueous hydrofluoric acid. Similar to the classical MXene, ideal Mo$_{4/3}$B$_2$ whose atomic arrangements based on the hexagonal i-MAB phase in space group $R\overline{3}m$ has three atom-layers. The discovery of a 2D transition metal boride not only suggests a wealth of future 2D materials that can be obtained through the chemical exfoliation of laminated compounds, but also indicates that 2D molybdenum boride may have other atomic structures. As shown in figure 1, middle layer is boronene as honeycomb and displayed as littler gray balls. The top and bottom Mo-layers are colored yellow and blue respectively, and the atoms in the overlapping parts of the two layers are colored half yellow and half blue. This approach is used throughout this paper to label the atomic arrangement of all 2D molybdenum boride models.

We employed first-principles plane-wave pseudopotential (PW-PP) method to calculate the binding energies of the bulk Mo and B firstly, the results were 6.36 eV/atom and 6.28 eV/atom, respectively. The experimentally measured binding energies of bulk Mo and B are 6.82 eV/atom and 5.84 eV/atom, respectively, and the comparison shows that the errors of the calculations are about 7%, which verifies the reliability of the results in this work. The symmetrical structures of the top and bottom Mo-layers were considered, which led to three different atomic structures, as shown in figure 2. The atomic arrangement of the Mo-layers in these three models was referenced to the 3D i-MAB phase. The Mo-layers in the configuration shown in figure 2(a) have honeycomb arrangement similar to that of i-MAB phase. In addition to this, the models without metal vacancies and with more metal vacancies, as shown in figures 2(b) and (c), can be obtained by taking into account the stripping and readsortion of the Mo atoms. In addition, the Arabic numbers in the figures indicate the numbering of the models about different molybdenum boride structures. The binding energies of these three models calculated by first-principles are listed in table 1. This result suggests that 2D molydbdenum borides with conventional MXene structures without metal vacancies have the largest binding
energy. A comparison of the binding energies of the three different structures shows that the higher the Mo content in 2D molybdenum boride, the larger the binding energy. On the other hand, we note that the binding energy per atom traditionally used to describe the stability and the binding strength of systems with unequal ratios of atomic number and atomic type is inaccurate. Therefore, we further propose to assess the stability of the system in terms of the binding energy per unit area (for 2D materials). In this way, the unit area is used as a uniform standard to compare the binding energy of different structures. As shown in Table 1, even with this criterion, the positive effect of Mo atomic number on the stability of 2D molybdenum boride is also demonstrated. In addition, the lattice constants for the different models are listed also in the table. It is worth noting that the six-membered B rings occupied by Mo atoms expands due to Mo’s large atomic radius, which results in a larger lattice constant for molybdenum boride with higher Mo content.

Table 1. The total energy, atomic number, and binding energy for $2 \times 2 \times 2$ supercell for models 1, 2 and 3 at 0 K. The values of energies with more than 2 significant digits will be truncated.

| Model number | Total energy (eV) | Total number of B | Total number of Mo | Binding energy (eV/atom) | Binding energy (eV/Å$^2$) | lattice constants (Å) |
|--------------|------------------|------------------|--------------------|-------------------------|---------------------------|-----------------------|
| Mo$_4$/3B$_2$ 1 | $-76.95$ | 6 | 4 | 4.77 | 1.77 | 5.19 |
| Mo$_2$B$_2$ | $-101.38$ | 6 | 6 | 5.94 | 2.52 | 5.32 |
| Mo$_2$/3B$_2$ | $-55.49$ | 6 | 2 | 3.39 | 1.02 | 5.16 |

Figure 3. The models with top and bottom Mo atoms asymmetrically arranged at the center of six-membered B rings. The Arabic number in the top left corner of each model is the model serial number.

Figure 4. The molybdenum boride conformation with only one Mo-layer at the bottom. The Arabic number in the top left corner of each model is the model serial number.
On the other hand, the possible structures of the system become very complex when the top and bottom metal atoms are asymmetrically arranged. Two Mo-layers with the same arrangement of Mo atoms but asymmetrical around boronene form a staggered honeycomb structure as shown in figure 3(a), resulting in a 2D molybdenum boride that is also the ideal structure Mo$_{4/3}$B$_2$ suggested by Zhou et al\cite{20}. Furthermore, the five other molybdenum boride models can be obtained, as shown in figures 3(b)–(f), based on the arrangement of the atoms in the Mo-layers in figure 2. The results of the binding energy for the six 2D molybdenum boride models shown in figure 3 are listed in table 2, where the different structures exhibit significant differences. The table shows that the model with least Mo content of Mo$_{2/3}$B$_2$ has the lowest binding energy and the model with the most Mo content of Mo$_{5/3}$B$_2$ has the largest binding energy. It is worth noting that the experimentally synthesized molybdenum boride, Mo$_{4/3}$B$_2$, does not have the largest binding energy in these six structures, suggesting that it is not the most stable structure in terms of binding energy. In addition, the binding energies of the molybdenum borides shown in figure 3 also exhibit a larger binding energy with increasing Mo content.

When considering the situation only existing one Mo-layer in the molybdenum boride structure, the structure models with a single Mo-layer were constructed based on the ones with double Mo-layer in figure 2 as shown in figure 4. The binding energies of three structures with a single Mo-layer are listed in table 3, again showing that the higher Mo content the larger the binding energy. Despite that MoB$_2$ (model 11) has the same Mo content as MoB$_2$ (model 7), MoB$_2$ (model 11) with Mo atoms occupying the center of all the six-membered B rings exhibits the larger binding energy.

The above calculated binding energies show that the Mo content in the 2D molybdenum borides has an important influence on their structural stability. In order to show the difference in stability between the twelve

| Model number | Total energy (eV) | Total number of B | Total number of Mo | Binding energy (eV/atom) | Binding energy (eV/Å$^2$) | lattice constants (Å) |
|--------------|------------------|------------------|-------------------|--------------------------|---------------------------|----------------------|
| Mo$_{4/3}$B$_2$ 4 | $-77.68$ | 6 | 4 | 4.85 | 1.82 | 5.17 |
| Mo$_{2/3}$B$_2$ 5 | $-55.02$ | 6 | 2 | 3.33 | 0.97 | 5.23 |
| Mo$_{5/3}$B$_2$ 6 | $-89.96$ | 6 | 5 | 5.48 | 2.20 | 5.24 |
| MoB$_2$ 7 | $-66.29$ | 6 | 3 | 4.17 | 1.43 | 5.13 |
| Mo$_{4/3}$B$_2$ 8 | $-79.01$ | 6 | 4 | 4.98 | 1.86 | 5.17 |
| MoB$_2$ 9 | $-66.40$ | 6 | 3 | 4.18 | 1.38 | 5.23 |

| Model number | Total energy (eV) | Total number of B | Total number of Mo | Binding energy (eV/atom) | Binding energy (eV/Å$^2$) | lattice constants (Å) |
|--------------|------------------|------------------|-------------------|--------------------------|---------------------------|----------------------|
| Mo$_{2/3}$B$_2$ 10 | $-55.68$ | 6 | 2 | 3.41 | 0.92 | 5.44 |
| MoB$_2$ 11 | $-68.06$ | 6 | 3 | 4.36 | 1.55 | 5.04 |
| Mo$_{1/3}$B$_2$ 12 | $-44.68$ | 6 | 1 | 2.39 | 0.59 | 5.34 |

Figure 5. Binding energy comparison of the twelve 2D molybdenum boride models.
models, the binding energies of these models are compared in figure 5, which shows that the metal vacancies, particularly those without any Mo atoms at the center of the six-membered B rings, reduces the stability of the system. Among the twelve 2D molybdenum boride models the binding energies of those with the same Mo content are relatively close but differ. For example, although the models 1, 4 and 8 have the same Mo content \((\text{Mo}_4/3\text{B}_2)\), model 1 with the metal vacancies that is the absence of any Mo atoms at the center of the six-membered B rings has the minimum binding energy, while model 8, where the metal vacancies occupy only one Mo layer, has the largest binding energy. These results suggest that not only the Mo content but also the differences in vacancy positions caused by the atomic arrangement affect the stability of the system.

On the other hand, 2D \(\text{Mo}_{4\,3/3}\text{B}_2\) obtained by selective etching from the 3D \(\text{i-MAB}\) phase would, ideally, exhibit ordered Mo vacancies. However, the experimentally STEM images [20] indicate the presence of other
atomic structures, implying the stripping and redesorption of Mo atoms. As shown in figure 6, we further simulated the STEM images of different models and compared them with the experimentally STEM images [20]. The figure shows that the simulated STEM images of the four models with the largest binding energies among the twelve can match with some part of the images directly from the experiment. It is worth noting that models 4 and 8 (Mo4/3B2) not only have the same Mo content and similar binding energies but also have very similar STEM images because of the atomic arrangement, as shown in figures (a) and (c). Our binding energy calculations show that Mo4/3B2 is not the most stable 2D molybdenum boride structure, which is also reflected in the experimental STEM observation.

Thus, the present study shows that the adsorptions of Mo in the center of the six-membered B rings improves the stability of 2D molybdenum boride. In order to further investigate the mechanism of Mo content affecting the stability of the system, the electron localization function (ELF) of 2D molybdenum boride was calculated to analyze the bonding property. The top-view and side-view ELF figures of 2D Mo4/3B2 (model 4) with metal vacancies are presented in figures 7(a) and (b), respectively. The isosurface of top-view ELF in figure 7(a) exhibits a clear electron localization between the B-B atomic pairs, suggesting that the B-B bonds are covalent bond [36, 37]. The side-view ELF of the crystal plane in the red dashed rectangular area in figure 7(a) is presented in figure 7(b) to demonstrate the bonding state of the Mo–B bonds. It is noteworthy that the ELF at the Mo atom is approximately equal to 0, as shown in figure 7(b), indicating that there is charge transfer from Mo to B in Mo–B bond [23, 38, 39]. As a result, the Mo–B bond is an ionic bond [36]. Our binding energy calculations show that the Mo4/3B2 is not the most stable structure in the 2D molybdenum boride series. Therefore, we also calculated the ELF of MXene type Mo2B2 (model 2), as shown in figures 7(c) and (d) for comparison. The figures 7(b) and (d) reveals that the electron localization at the B–B bonds and around the B atoms in Mo2B2 are higher than that in Mo4/3B2. Moreover, the maximum value of ELF at B–B bonding in Mo2B2 is 0.76 while that in Mo4/3B2 is 0.72. This indicates that the B–B bondings in Mo2B2 are significant stronger than that in Mo4/3B2.

The presence of metal vacancies leads to differences in the strength of the B–B bonds at different positions in the Mo4/3B2, which cause alternating lengths in the B–B bonds. In contrast, the bond strengths of each B–B bond in the Mo3B2 are more homogeneous. On the other hand, the B–B bonds of Mo2B2 has stronger electron localization than that of Mo4/3B2, as shown in figures 7(a) and (c), which indicates that the increase of Mo content further strengthens the B–B bonds. This enhancement is attributed to the charge transfer from Mo to B in Mo–B ion-bond. As a result, both the binding energies and the ELFs suggest that Mo at the six-membered B rings can strengthen the stability of 2D molybdenum boride, which also reveals the reason for the existence of variable atomic structures in Mo4/3B2−x.

4. Conclusions

Two-dimensional metal borides Mo4/3B2−x synthesized experimentally by selective etching from the 3D i-MAB phase have further extended the family of two-dimensional materials. Ideally the 2D Mo4/3B2 obtained would have ordered metal vacancies, however, experimental observation of the STEM image shows that there are variable atomic structures in the system. In the present work, twelve molybdenum boride models have been constructed based on the atomic arrangement of the 3D i-MAB phase and their stability has been investigated by first-principles calculations. As the results, the binding energies of the twelve 2D molybdenum boride models shown that a higher Mo content results in a larger binding energy, meaning that the greater stability of the 2D molybdenum boride. Furthermore, the binding energy calculations shown that the 2D Mo4/3B2 structure is not the most stable structure among these models. The atomic structures of the four most stable models among these models can be directly matched to the experimental STEM images. The results of ELF show that the strength of the B–B bonds in 2D molybdenum boride are significantly stronger than that of the Mo–B bonds. The MXene type Mo2B2 has stronger bonding strength than that of the Mo4/3B2. In addition, ELF calculations show that the B–B bonds in 2D molybdenum boride are covalent-bond while its Mo–B bonds are ionic-bond. The increase of Mo content can significantly strengthen the B–B bonds. These results suggest that attention needs to be paid to the redesorption of Mo atoms at vacancies in the experimental studies and the practical applications of 2D molybdenum borides with ordered vacancies. This paper therefore reveals the reasons for the existence of multiple atomic structures in the experimentally synthesized 2D Mo4/3B2−x in terms of the energy and bonding properties, which is of significance as a guide for the synthesis and application of 2D metal borides.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of competing interest

The authors declare that no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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