The impact of hexagonal boron nitride encapsulation on the structural and vibrational properties of few layer black phosphorus

Magdalena Birowska¹, Joanna Urban², Michał Baranowski²,³, Duncan K Maude², Paulina Plochocka² and Nevill Gonzalez Szwacki¹

¹ University of Warsaw, Faculty of Physics, Pasteura 5, 02-093 Warsaw, Poland
² Laboratoire National des Champs Magnetiques Intenses, UPR 3228, CNRS-UGA-UPS-INS, Grenoble and Toulouse, France
³ Department of Experimental Physics, Faculty of Fundamental Problems of Technology, Wroclaw University of Science and Technology, Wroclaw, Poland

E-mail: Magdalena.Birowska@fuw.edu.pl

Received 21 November 2018, revised 23 January 2019
Accepted for publication 30 January 2019
Published 28 February 2019

Abstract

The encapsulation of two-dimensional layered materials such as black phosphorus is of paramount importance for their stability in air. However, the encapsulation poses several questions, namely, how it affects, via the weak van der Waals forces, the properties of the black phosphorus and whether these properties can be tuned on demand. Prompted by these questions, we have investigated the impact of hexagonal boron nitride encapsulation on the structural and vibrational properties of few layer black phosphorus, using a first-principles method in the framework of density functional theory. We demonstrate that the encapsulation with hexagonal boron nitride imposes biaxial strain on the black phosphorus material, flattening its puckered structure, by decreasing the thickness of the layers via the increase of the puckered angle and the intra-layer P–P bonds. This work exemplifies the evolution of structural parameters in layered materials after the encapsulation process. We find that after encapsulation, phosphorene (single layer black phosphorous) contracts by 1.1% in the armchair direction and stretches by 1.3% in the zigzag direction, whereas few layer black phosphorus mainly expands by up to 3% in the armchair direction. However, these relatively small strains induced by the hexagonal BN, lead to significant changes in the vibrational properties of black phosphorus, with the redshifts of up to 10 cm⁻¹ of the high frequency optical mode A₁g. In general, structural changes induced by the encapsulation process open the door to substrate controlled strain engineering in two-dimensional crystals.

Keywords: density functional theory, 2D materials, vdW heterostructures, Raman spectra, black phosphorus

(Some figures may appear in colour only in the online journal)

Introduction

Two-dimensional (2D) materials offer novel physics and potential use in multiple applications [1–6]. However, many of the layered materials are very sensitive to the local environment and ambient conditions [7–14]. Black phosphorus (BP) represents an extreme example of sensitivity to moisture and oxygen which can lead to catastrophic degradation on a time scale of only minutes [15–17]. Therefore, to utilize its distinctive anisotropic properties in electronic,
optoelectronic and thermo-electronic applications [18–25], methods of BP stabilization are unavoidable [26, 27]. Recent studies have shown that encapsulation with hexagonal boron nitride (hBN) protects BP from structural and chemical degradation, while improving its electrical properties [28–32] making hBN the most commonly used material for encapsulation. In contrast to other layered 2D materials such as transition metal dichalcogenides (TMDs) and graphene in BP the bonding between the consecutive layers is not purely of the van der Waals type [33]. In BP atoms forms covalent bonds with three intralayer neighbors leaving a pair of lone electrons dangling out into the interlayer vacuum region [34, 35]. This results in enhanced interlayer interaction giving rise to a strong thickness dependence of the band gap [36] and is also the main reason for the strong surface reactivity in air. In addition, it has been recently shown that in graphene-phosphorene heterostructures a large in-plane lattice contraction in phosphorene is induced, leading to a strong modification of the structural and electronic properties [37].

It is therefore expected that the encapsulation of BP with hBN should affect its lattice structure. Since encapsulation is crucial to stabilize BP based devices, it is important to understand the interaction of BP with encapsulating materials. In addition, the detailed exploration of the structural and vibrational properties can expand our understanding on the lattice vibrations in this family of largely unexplored van der Waals heterostructures.

In this paper we examine the influence of hBN encapsulation on the structural and vibrational properties of BP using density functional theory (DFT). We show that encapsulation strains the BP layer which has significant impact on the vibrational properties. Both non-encapsulated and encapsulated BP layers, exhibit anomalous evolution of phonon frequencies, which show a redshift with increasing number of layers. Encapsulation further enhances this redshift. Our studies shows that the underlying reason for this is the biaxial strain exerted on the hBN encapsulated BP layers which modifies the vibrational frequencies. The presented theoretical predictions are in good agreement with the results of Raman spectroscopy performed on hBN encapsulated BP. Our results shows that the presence of enhanced interlayer interaction in BP open the door to substrate controlled strain engineering in 2D crystals.

**Methodology**

**Experimental details**

The experimental results for hBN encapsulated BP presented in this work are based on data published and discussed in [38]. All the details about the experimental setup and sample preparation can be also found in [38].

| Structures     | LDA                        | OptB86b-vdW                  |
|----------------|----------------------------|-----------------------------|
|                | $d$ (Å)  | $E_b$ (meV Å$^{-2}$) | $d$ (Å)  | $E_b$ (meV Å$^{-2}$) |
| 2L of BP       | 2.90    | 26.04           | 3.12    | 30.57             |
| 2L of graphene | 3.31    | 9.97            | 3.31    | 24.79             |
| hBN-BP         | 3.30    | 10.32           | 3.42    | 21.73             |
| hBN-graphene   | 3.50    | 2.84            | 3.50    | 16.86             |

**Table 1.** Equilibrium distances, $d$, and interlayer binding energies, $E_b$, for several structures. Positive values of energies indicate stable structures.

**Computational approach**

The calculations were performed in the framework of DFT, within the local density approximation (LDA), [39] as implemented in the Quantum Espresso package [40]. The electron-ion interaction was modeled using norm-conserving pseudopotentials [41]. The kinetic energy cutoff for the plane-wave expansion of the pseudo-wave function was set to 60 Ry. A k-mesh of $15 \times 12 \times 1$ was taken to sample the Brillouin zone of the conventional unit cell for few layer BP. To do the slab calculations a 16 Å of vacuum is added in order to avoid spurious interactions between replicates. The lattice parameters of each of the supercell were fully optimized and all of the atoms were relaxed until the maximal force per atom was less than $10^{-3}$ eV Å$^{-1}$. With the optimized structures and self-consistent wave functions the phonon spectra and Raman intensities (non-resonant Raman) were calculated as introduced by Lazzeri and Mauri [42]. Density functional perturbation theory (DFPT) [43] was employed to obtain phonon related properties. The threshold for the self-consistency of the DFPT was set to $10^{-14}$.

It was recently shown that the interlayer interaction between the layers of BP is not simply of the weak van der Waals type [34]. There exists sizable covalent interactions between the phosphorene layers significantly greater than for the other 2D materials such as graphene or MoS$_2$ [34]. In order to quantify the character of the interlayer bonding between the interface of hBN and BP layers, we calculate the interlayer binding energies as well as the interlayer equilibrium distances, for several structures; a bilayer of BP, a bilayer of graphene, hBN-BP, and hBN-graphene. All of the calculated values are collected in table 1. We have employed two different exchange-correlation functionals, traditional LDA and optB86b-vdW [44] which takes into account the van der Waals interactions. The energetics or the interlayer distances can be well reproduce using the appropriately chosen vdW exchange-correlation functional. The OptB86b is one of the several vdW functional proposed which are computationally cheaper than the highly computationally demanding RPA method [45, 46]. The latter is considered to be one of the most accurate methods for describing the physics of vdW materials [45, 47].

The interlayer distances between the graphene and phosphorene layers (see table 1) are reasonably well predicted by the LDA approach. In general the LDA approach correctly
described the chemical covalent bonds, however, for fortuitous reasons it can also reproduce quite well the interlayer distances in layered materials [48]. Similar results have been previously obtained by using different codes [48] and van der Waals type of functional [34]. The interaction between the graphene layers are strongly underestimated by the LDA approach, the predicted interlayer binding energy is 9.97 meV Å⁻² compared to the correct value of 24.79 meV Å⁻² when van der Waals interactions are taken into account. In case of two layer BP the LDA and optB86b-vdW approaches give similar values, of 26.04 meV Å⁻² and 30.57 meV Å⁻², respectively, indicating the rather quasicovalent character of the bonding [34]. This suggests that the LDA approach should capture most of the relevant physics of the interaction between the BP layers. In contrast, the LDA calculations clearly underestimate the binding energy for two layer graphene, hBN-BP and hBN-graphene showing the importance of the van der Waals interaction in these system. We note that a similar value 21.6 meV Å⁻² for hBN-BP [49] has been previously obtained using a different type of vdW exchange-correlation functional.

For our detailed calculations on hBN encapsulated few layer BP we have decided to use the LDA approach which provides the best description of the interlayer phonon frequencies [34]. The encapsulation process in our calculations is captured by introducing biaxial strain directly calculated for the hBN-BP-hBN heterostructures. Due to the weak van der Waals forces we expect no changes in electronic structures [48] or negligible charge transfer at the interface [50], which justifies our approach. We use the smaller (1 × 1) lateral supercell of BP layers, where the strains are respectively rescaled. The BP strained supercells, are then used to calculate the vibrational properties.

Structural properties of freestanding and encapsulated BP layers

The epitaxy of hBN/BP/hBN imposes the hexagonal structure of BN on the orthogonal superlattice of BP layers. This is in contrast to widely examined 2D heterostructures such as graphene/TMD, graphene/BN, graphene/silicene, TMD/TMD, where the constituent layers possess the same hexagonal lattice structure. Therefore, each supercell is constructed by combining an orthogonal (√3 × 1) supercell of hBN and (3 × 1) supercell of phosphorene (see figure 1) [50]. Note, that there is a lack of experimental data concerning the arrangements of the hBN and BP layers. Thus, it is possible, that the mutual alignment of the hBN and BP layers in the chosen supercell differs from reality.

In figures 2(a) and (b), we present the results of lattice parameters for the bare BP layers (black curve) and encapsulated BP layers⁴ (red curve). Our results for the bare structures show clear trends of the in-plane lattice parameters, namely, a large decrease in armchair lattice constant by about 0.20 Å with increasing number of layers, accompanied by a much smaller increase of 0.03 Å of the zigzag lattice constant. Similar trends were previously obtained for few layers with the vdW approach [33]. In contrast the encapsulated BP layers show a small decrease in the lattice parameters as the function of the number of the layers for both in-plane directions, indicating that the BP layers are significantly strained by the hBN encapsulation.

In order to quantify this effect, we calculate the biaxial strains for both hBN encapsulated BP layers and the hBN layer itself (see figures 2(c) and (d)). We define the uniaxial strain along zigzag (or armchair) direction for a given number nL of BP layers as

$$\epsilon_{BP} = \frac{a_{n}^{\text{BP}} - a_{0}^{\text{BP}}}{a_{n}^{\text{BP}}} \times 100\%,$$

and for the hBN encapsulated layer as

$$\epsilon_{hBN} = \frac{a_{n}^{\text{hBN}} - a_{0}^{\text{hBN}}}{a_{n}^{\text{hBN}}} \times 100\%,$$

where $a_{n}^{\text{BP}}$ and $a_{0}^{\text{BP}}$ denote the optimized lattice constants of encapsulated (e-BP) and bare (b-BP) optimized n-layer BP structures, whereas $a_{n}^{\text{hBN}}$ indicates a single layer of hBN used to encapsulate the n BP layers (n = 0 corresponds to bare hBN). Positive and negative values of $\epsilon$ correspond to tensile and compressive strains.

Figures 2(c) and (d) show the strain of the examined structures as a function of the number of BP layers. The capping hBN layer is weakly compressed, and this compression slightly increases with the number of BP layers up to 0.52% and 0.4% for the zigzag and armchair directions, respectively. In striking contrast to the capping layer, the BP layers are tightly stretched (except for single layer BP in the
armchair direction) reaching value of 2.83% and 1.34%, for five layer BP in armchair and single layer BP in the zigzag directions, respectively. These results reveal the well known fact that hBN is a very stiff material, and hence, it enforces its own lattice structure on the entire vdW heterostructure.

We now calculate how the encapsulation via the induced lattice strain changes the structural parameters of the constituent BP layers. The results are illustrated in figure 3, where the black curves represent the freestanding BP layers, and red curves, the encapsulated ones. Under the encapsulation process the thickness of the BP layer (see figure 3(b)) decreases by about 0.015 Å, whereas the length of the in-plane intralayer bond increases by approximately 0.007 Å (see figure 3(c)) which is accompanied by an increase of the pucker angle $\theta$ of $\approx 0.8^\circ$ (see figure 3(f)). At the same time, the length of the interlayer bond remains almost unchanged (see figure 3(d)). These results clearly indicate that the encapsulation process flattens the puckered structure of the BP layers via an the expansion of the intralayer bonds (see figure 3(c)). Moreover, in all of the structural parameters a splitting into two branches is observed, which directly distinguish the atoms on the surface (lower branch) and the atoms in the inner layers (upper branch).

In addition, an extraordinary stretchability along the armchair direction of the hBN encapsulated BP layers is observed.

![Figure 2](image)

**Figure 2.** Dependence of lattice parameters on the number of BP layers (on the left) and the strain effect in the encapsulated layers (on the right) presented for the in-plane directions. In the (c) and (d) panels the strains are presented for the BP layers (black curve) and hBN layer (green curve) in the encapsulated BP structures. A large stretchability along the armchair direction of the hBN encapsulated BP layers is observed.

Vibrational properties of bare and encapsulated BP layers

Now we will present results, which show that the structural changes can significantly affect the vibrational properties of the vdW heterostructures. Although the vibrational properties of 2D structures such as graphene, transition metal dichalcogenides (TMDs) or BP are well studied, the vibrational properties of vdW heterostructures remain largely unexplored. Here we focus on the $A_{1g}$ optical intralayer mode for which encapsulation produces the most pronounced vibrational changes observed experimentally [38]. For the other intralayer modes such as $A_{2g}$ and $B_{2g}$ the calculated frequencies do not significantly change upon encapsulation. The intralayer modes involve the vibrations from the in-plane chemical bonding, and thus, can give insight into these bonds [52].
Here we present the results of the hBN encapsulation as a function of the number of BP layers, by taking into account the biaxial strains resulting from hBN capping layers. This aspect is the main difference between our and previously reported results under the strain \cite{33, 53, 54}. In previous studies concerning vibrational properties, mostly the phonon frequencies were examined. In this work we also present the theoretical predictions and experimental results for the non-resonant Raman intensities.

Recently it has been shown that the evolution of the frequency modes is anomalous, namely a redshift in frequency is observed with an increasing number of layers, \cite{38, 55} in contrast to weakly coupled 2D materials where a blueshift is predicted \cite{56}. An obvious question is can this anomalous behavior in encapsulated layers be easily understood in terms of the structural changes, as suggested in \cite{33} or if a different mechanism has to be considered.

All of the results presented here are calculated for (1 × 1) supercell, and the encapsulation effect is included by taking into account the biaxial strain introduced by the presence of the hBN layers. The strain depends strongly on the thickness of the examined vdW heterostructures. Figure 4 shows the evolution of the \( A_1 \) high frequency mode for theoretical and experimental results. Both, theory and experiment results, exhibit similar trends, namely two branches (a splitting) are observed for three layers and above.

The frequency splitting originates from the different stiffness of the surface and inner layers. The surface layer is stiffer in comparison to inner layers for both bare and encapsulated structures, which is revealed by the different structural parameters of surface atoms compared to atoms in the inner layers. Namely, intralayer and interlayer bonds (see figures 3(c) and (d)), the interlayer spacing (figure 3(a)) and the layer thickness (figure 3(b)) are all reduced for atoms at the surface. This reflects the stronger attraction between atoms from surface layers than between atoms from inner layers, independently of whether we are dealing with bare or encapsulated BP layers.

In addition, the encapsulation process can significantly decreases the frequency of the studied modes, and this decrease strongly depends on the thickness of the structures reaching a value of 10 cm\(^{-1}\) for single layer BP and minimum value of 2 cm\(^{-1}\) for two layer BP in comparison to free-standing BP layers (see figure 4(d)). The origin of this redshift stems from the increase of the interlayer spacing (red curve in comparison to black curve in figure 3(a)), which results in smaller attraction between the layers, as well as the lateral extension of the puckered structure of BP layers via the increased pucker angle (see figure 3(f)) and the elongation of the intralayer bonds (see figure 3(c)).

**Experiment versus theory**

Both, theoretical as well as the experimental results, for encapsulated layers exhibit similar trends for the evolution of the \( A_1 \) mode (see figure 4), namely two branches are observed for three layers and above. The Raman measurements (red curve in figure 4(b)) were carried out for encapsulated BP layers. No splitting for non-encapsulated BP has been reported, in contrast to to theoretical results, which also predict splitting for bare phosphorus. This can be understood as a result of material quality improvement after encapsulation and
narrowing of the observed modes \[38\] which facilitates detection of the elusive peak.

In addition, both the experimental and theoretical results show that the most pronounced elusive peak\(^5\) is observed for three layers (3L), and its intensity decreases with the number of the BP layers in the system (see figure 5). This effect can be understood in terms of the relative number of atoms at the surface (origin of elusive peak), compared to the number of atoms present in inner layers (origin of the main peak), as the Raman intensity is proportional to the number of atoms in the system. In case of three layers, there exists the largest ratio for the number of surface atoms to number of inner atoms. Therefore, the elusive peak is quite strong for three layers, and its intensity monotonically decreases with the increase of the layers in the systems. Moreover, for the most pronounced case (3L), the elusive peak can be even slightly enhanced by encapsulation process (see figure 5), and from the Raman intensity point of view, it can be easier to detect in experiment.

Surprisingly the theoretical results shows that after encapsulation the energy of the https://www.overleaf.com/21294815qngzjchgsqg $A_g^1$ mode decreases for all number of layers. This is in contrast to experimental results where hBN encapsulation leads to an $A_g^1$ frequency which is higher than in non-encapsulated samples (see figures 4 (b), (e)). However, non-encapsulated BP is not actually freestanding as in all reports BP structure are placed on some kind of substrate, usually on SiO\(_2\). The SiO\(_2\) is much more ‘rugged’ than hBN and possesses a large number of dangling bonds so it is expected that its interaction with BP is stronger than hBN increasing the value of the strain redshifting the $A_g^1$ mode. It is worth to note that this argumentation leads to the conclusion that all of the so far reported studies have been in fact performed on the strained BP. Hence the further experimental and theoretical studies are highly needed and desirable in this aspect.

Conclusions

In conclusion we have performed detailed theoretical studies of the vibrational properties of bare and hBN encapsulated with BP. We have shown, that the strong interaction between the individual layers of BP results in different stiffness of the surface and inner layers. This is directly reflected by the splitting of the $A_g^1$ Raman mode for three layer and above BP. Furthermore, we have demonstrated that the strain of the BP is strongly affected by the encapsulating layer. In particular we show that the commonly used hBN encapsulation has a significant impact on the vibrational properties of the BP layers. Namely, the $A_g^1$ interlayer mode frequencies decrease by $\approx$(2–10) cm\(^{-1}\) compared to bare BP (depending on the number of layers). This redshift results from the smaller attraction between the layers as well as and flattening of the
puckered structure of BP via the extension of the intralayer bonds and the pucker angle. Our theoretical prediction are in good quantitative agreement with experimental results. Importantly, our calculations reveal that in case of BP even van der Waals interaction of BP with encapsulating material can significantly affects its properties due to strain formation. This interaction can be become even more important in case of less 'flat' substrate and the influence of the encapsulation layer and cannot be neglected. The result of this study provide a starting point to define a strategy for the strain engineering in BP based heterostructures.

Acknowledgments

This work is funded by the National Science Center grant no. UMO-2016/23/D/ST3/03446. Access to computing facilities of PL-Grid Polish Infrastructure for Supporting Computational Science in the European Research Space and of the Interdisciplinary Center of Modeling (ICM), University of Warsaw is gratefully acknowledged. The experimental work was partially supported by BLAPHENE and STRABOT projects, which received funding from the IDEX Toulouse, Emergence program, ‘Programme des Investissements d’Avenir’ under the program ANR-11-IDEX-0002-02, reference ANR-10-LABX-0037-NEXT, and by the PAN-CNRS collaboration within the PICS 2016-2018 agreement. We thank EPSRC for funding through grant EP/M05173/1. Michal Baranowski appreciates support from the Polish Ministry of Science and Higher Education within the Mobilnosc Plus program (grant no. 1648/MOB/V/2017/0). NGSz gratefully acknowledges the support of the National Science Centre through grant no. UMO-2016/23/B/ST3/03575.

ORCID iDs

Magdalena Birowska @ https://orcid.org/0000-0001-6357-7913
Joanna Urban @ https://orcid.org/0000-0003-0714-7753
Michal Baranowski @ https://orcid.org/0000-0002-3320-2069
Paulina Plochocka @ https://orcid.org/0000-0002-4019-6138
Nevill Gonzalez Szwacki @ https://orcid.org/0000-0002-0518-844X

References

[1] Tan C et al 2017 Recent advances in ultrathin two-dimensional nanomaterials Chem. Rev. 117 6225–331
[2] Fiori G et al 2014 Electronics based on two-dimensional materials Nat. Nanotechnol. 9 768
[3] Xu X, Yao W, Xiao D and Heinz T F 2014 Spin and pseudospins in layered transition metal dichalcogenides Nat. Phys. 10 343
[4] Geim A K and Grigorieva I V 2013 Van der Waals interactions in two-dimensional materials Energy Environ. Sci. 6 183–201
[5] Ling X, Wang H, Huang S, Xia F and Dresselhaus M S 2015 The renaissance of black phosphorus Proc. Natl Acad. Sci. 201514681
[6] Carvalho A et al 2016 Phosphorene: from theory to applications Nat. Rev. Mater. 1 10061
[7] Zhou S, Y et al 2007 Substrate-induced bandgap opening in epitaxial graphene Nat. Mater. 6 770
[8] Wang Y Y et al 2008 Raman studies of monolayer graphene: the substrate effect J. Phys. Chem. C 112 10637–40
[9] Calizo I, Bao W, Miao F, Lau C N and Balandin A A 2007 The effect of substrates on the raman spectrum of graphene: Graphene-on-sapphire and graphene-on-glass Appl. Phys. Lett. 91 201904
[10] Tongay S et al 2013 Defects activated photoluminescence in two-dimensional semiconductors: interplay between bound, charged, and free excitons Sci. Rep. 3 2657
[11] Tongay S et al 2013 Broad-range modulation of light emission in two-dimensional semiconductors by molecular physisorption gating Nano Lett. 13 2831–6
[12] Zhang W et al 2013 High-gain phototransistors based on a cvd MoS2 monolayer Adv. Mater. 25 3456–61
[13] Raja A et al 2017 Coulomb engineering of the bandgap and excitons in two-dimensional materials Nat. Commun. 8 15251
[14] Ster A V, Wilson N P, Clark G, Xu X and Crooker S A 2016 Probing the influence of dielectric environment on excitons in monolayer WSe2: insight from high magnetic fields Nano Lett. 16 7054–60
[15] Favron A et al 2015 Photooxidation and quantum confinement effects in exfoliated black phosphorus Nat. Mater. 14 826
[16] Castellanos-Gomez A et al 2014 Isolation and characterization of few-layer black phosphorus 2D Materials 1 025001
[17] Koenig S P, Doganov R A, Schmidt H, Castro Neto A and Ozyilmaz B 2014 Electric field effect in ultrathin black phosphorus Appl. Phys. Lett. 104 103106
[18] Li L et al 2014 Black phosphorus field-effect transistors Nat. Nanotechnol. 9 372
[19] Fei R et al 2014 Enhanced thermoelectric efficiency via orthogonal electrical and thermal conductances in phosphorene Nano Lett. 14 6393–9
[20] Luo Z et al 2015 Anisotropic in-plane thermal conductivity observed in few-layer black phosphorus Nat. Commun. 6 8572
[21] Guo Z et al 2015 From black phosphorus to phosphorene: basic solvent exfoliation, evolution of raman scattering, and applications to ultrafast photonics Adv. Funct. Mater. 25 6996–7003
[22] Qiao J, Kong X, Hu Z-X, Yang F and Ji W 2014 High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus Nat. Commun. 5 4475
[23] Wang X et al 2015 Highly anisotropic and robust excitons in monolayer black phosphorus Nat. Commun. 10 517
[24] Zhang S et al 2014 Extraordinary photoluminescence and strong temperature/angle-dependent raman responses in few-layer phosphorene ACS Nano 8 9590–6
[25] Liu S et al 2015 Thickness-dependent Raman spectra, transport properties and infrared photophone of few-layer black phosphorus J. Mater. Chem. C 3 10974–80
[26] Wood J D et al 2014 Effective passivation of exfoliated black phosphorus transistors against ambient degradation Nano Lett. 14 6964–70
[27] Na J et al 2014 Few-layer black phosphorus field-effect transistors with reduced current fluctuation ACS Nano 8 11753–62
[28] Doganov R A et al 2015 Transport properties of ultrathin black phosphorus on hexagonal boron nitride Appl. Phys. Lett. 106 083505
[29] Cao Y et al 2015 Quality heterostructures from two-dimensional crystals unstable in air by their assembly in inert atmosphere Nano Lett. 15 4914–21
[30] Chen X et al 2015 High-quality sandwiched black phosphorus heterostructure and its quantum oscillations Nat. Commun. 6 7315
[31] Long G et al 2016 Achieving ultrahigh carrier mobility in two-dimensional hole gas of black phosphorous Nano Lett. 16 7768–73
[32] Arsva A et al 2015 Air-stable transport in graphene-contacted, fully encapsulated ultrathin black phosphorus-based field-effect transistors ACS Nano 9 4138–45
[33] Hu Z-X, Kong X, Qiao J, Normand B and Ji W 2016 Interlayer electronic hybridization leads to exceptional thickness-dependent vibrational properties in few-layer black phosphorus Nanoscale 8 2740–50
[34] Luo X et al 2015 Large frequency change with thickness in interlayer breathing mode–significant interlayer interactions in few layer black phosphorus Nano Lett. 15 3931–8
[35] Hu Z-X, Kong X, Qiao J, Normand B and Ji W 2016 Interlayer electronic hybridization leads to exceptional thickness-dependent vibrational properties in few-layer black phosphorus Nanoscale 8 2740–50
[36] Li L et al 2017 Direct observation of the layer-dependent electronic structure in phosphorene Nat. Nanotechnol. 12 21
[37] Van Troeye B, Lherbier A, Charlier J-C and Gonze X 2018 Large phosphorene in-plane contraction induced by interlayer interactions in graphene-phosphorene heterostructures Phys. Rev. Mater. 2 074401
[38] Urban J M et al 2017 Observation of a1g raman mode splitting in few layer black phosphorus encapsulated with hexagonal boron nitride Nanoscale 9 19298–303
[39] Perdew J P and Zunger A 1981 Self-interaction correction to density-functional approximations for many-electron systems Phys. Rev. B 23 5048–79
[40] Giannozzi P and Stefano B 2009 Quantum espresso: a modular and open-source software project for quantum simulations of materials J. Phys.: Condens. Matter 21 395502
[41] Hamann D R 1989 Generalized norm-conserving pseudopotentials Phys. Rev. B 40 2980–7
[42] Lazzeri M and Mauri F 2003 First-principles calculation of vibrational raman spectra in large systems: signature of small rings in crystalline silicon Phys. Rev. Lett. 90 036401
[43] Baroni S, de Gironcoli S, Dal Corso A and Giannozzi P 2001 Phonons and related crystal properties from density-functional perturbation theory Rev. Mod. Phys. 73 515–62
[44] Klimeš J C V, Bowler D R and Michaelides A 2011 Van der waals density functionals applied to solids Phys. Rev. B 83 195131
[45] Mttendorfer F et al 2011 Graphene on n(111): strong interaction and weak adsorption Phys. Rev. B 84 201401
[46] Tawfik S A, Gould T, Stumpfl C and Ford M J 2018 Evaluation of van der waals density functionals for layered materials Phys. Rev. Mater. 2 034405
[47] Dobson J F 2014 Beyond pairwise additivity in london dispersion interactions Int. J. Quantum Chem. 114 1157–61
[48] Birowska M and Majewski K M 2011 Transport properties of ultrathin black phosphorus Nano Lett. 11 4138–45
[49] Rivero P et al 2015 Simulated scanning tunneling microscopy images of few-layer phosphorus capped by graphene and hexagonal boron nitride monolayers Phys. Rev. B 91 115413
[50] Cai G, Zhang Y and Zhang Y-W 2015 Electronic properties of phosphorene/graphene and phosphorene/hexagonal boron nitride heterostructures J. Phys. Chem. C 119 13929–36
[51] Qin Wei A X P 2014 Superior mechanical flexibility of phosphorene and few-layer black phosphorus Appl. Phys. Lett. 104 251915
[52] Ling X et al 2015 Low-frequency interlayer breathing modes in few-layer black phosphorus Nano Lett. 15 4080–8
[53] Tokar K, Derian J B R and Stich I 2016 Strain control of vibrational properties of few layer phosphorus Appl. Phys. Lett. 120 194305
[54] Fei R and Yang L 2014 Lattice vibrational modes and raman scattering spectra of strained phosphorene Appl. Phys. Lett. 105 083120
[55] Lu W et al 2014 Plasma-assisted fabrication of monolayer phosphorene and its raman characterization Nano Res. 7 853–9
[56] Lee C et al 2010 Anomalous lattice vibrations of single- and few-layer MoS2 ACS Nano 4 2695–700
[57] Phaneuf-L’Heureux A-L et al 2015 Polarization-resolved raman study of bulk-like and davydov-induced vibrational modes of exfoliated black phosphorus Nano Lett. 16 7761–7