Graphene-like quaternary compound SiBCN: A new wide direct band gap semiconductor predicted by a first-principles study

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Abstract – Due to the lack of two-dimensional silicon-based semiconductors and the fact that most of the components and devices are generated on single-crystal silicon or silicon-based substrates in modern industry, designing two-dimensional silicon-based semiconductors is highly desired. With the combination of a swarm structure search method and density functional theory in this work, a quaternary compound SiBCN with graphene-like structure is found and displays a wide direct band gap. The band gap is of $\sim 2.63$ eV which is just between $\sim 2.20$ and $\sim 3.39$ eV of the highlighted semiconductors SiC and GaN. Notably, the following calculation reveals that SiBCN possesses high carrier mobility with $\sim 5.14 \times 10^3$ and $\sim 13.07 \times 10^3$ cm$^2$ V$^{-1}$ s$^{-1}$ for electron and hole, respectively. Furthermore, the $ab$ initio molecular dynamics simulations also show that the graphene-like structure of SiBCN can be well kept even at an extremely high temperature of 2000 K. The present work tells that designing multicomponent silicides may be a practicable way to search for new silicon-based low-dimensional semiconductors which can match well with the previous Si-based substrates.

Introduction. – With the development of modern industry, device miniaturization is so desirable. Low-dimensional materials are just the ones that can satisfy this demand [1–3]. Besides, the properties of low-dimensional materials are always different from those of the bulk counterparts. For instance, graphite behaves as a common metal, while graphene is a zero-gap semiconductor with Dirac points [4,5]. Subsequently, motivated by the discovery of graphene, many researchers focus on exploring new low-dimensional monolayered materials via theoretical or experimental methods. As a result, many such materials have been reported, for example, h-BN sheet, borophene, phosphorene, germanene, silicene, two-dimensional (2D) transition metal dichalcogenides, and 2D transition metal dinitride, etc. [6–14].

On the other hand, semiconductors are so important for modern industry, such as in integrated circuit, power component, light-emitting diode (LED) fields and so on, thus it is necessary to search for 2D semiconducting materials. Up to date, some of such materials have been reported. For instance, hexagonal boron nitride (h-BN) with a gap of 5.8 eV is a representative one [15]. Atomically thin MoS$_2$ was also predicted as a direct-gap semiconductor in 2010 [16]. Few-layer black phosphorus was theoretically reported as a semiconductor with a direct gap which could increase up to 2.0 eV by decreasing the number of layers to one [17]. Recently in 2016, atomically thin InSe was reported as an indirect band gap semiconductor with a gap of $\sim 1.50$ eV [18]. However, despite many 2D semiconductors were found continuously, few works have reported on applications of these 2D semiconductors in the above-mentioned fields. We think that the main reason is that semiconducting materials are usually grown on Si or silicide substrates to date, while the most reported 2D semiconductors cannot match well with these substrates. Most recently, SiC and GaN have become the highlighted semiconducting materials because of their wide band gaps. However, SiC is an indirect bang gap semiconductor, single-crystal GaN is too expensive and there is still no suitable substrate for its growth.

The above fact encourages researchers to search for 2D silicon-based semiconductors. Silicene, as a 2D material with a buckling hexagonal honeycomb structure, was theoretically designed in 2009 [8]. The electronic calculation
shows that it exhibits a gapless semimetal, instead of a semiconductor like its bulk counterpart, and its charge carriers behave like a massless Dirac fermion due to the linear band crossing at the Fermi energy level ($E_F$). Following this prediction, some work was focused on tuning the band gap of silicene. For example, Du et al. regulated silicene from semimetal to semiconductor by chemically adsorbing oxygen atoms, and the band gap can range from 0.11 to 0.30 eV by tuning the adsorption configurations and amount of adsorbed oxygen atoms [19]. But, whether silicene with the oxygen atoms adsorbed on surface could match well with other silicon-based devices is an open question, because the adsorbed atoms would destroy the structure at the atomic level. Additionally, chemical modification is still hard to be achieved by experiment now. Besides, Ni et al. also theoretically predicted that silicene could be tuned to a semiconductor via a vertical electric field [20]. However, the electric field applied to open an effective gap is too high to achieve in experiment, especially in practical applications, for example, an electric field of 0.16 V/Å is required to open a gap of 0.026 eV. Therefore, searching for intrinsic semiconducting 2D silicides, instead of tuning silicene by different means, perhaps, can pave the way. Some metastable amorphous bulk SiBCN was reported with high thermal stability [21,22], 2D monolayer BCN was also predicted as a semiconductor [23], and Si is the element of the same group as C, indicating they have the same configuration of valence electrons. This fact motivates us to explore the possibility of the existence of 2D silicide SiBCN with semiconducting character. As expected, we theoretically designed a new wide direct band gap semiconductor—a hexagonal single-atom-thick quaternary compound SiBCN in this work.

**Computational methods.**—The structures employed herein are predicted by using the swarm-intelligence–based structural prediction calculations implemented in CALYPSO code. The code is developed to search for the stable structures of compounds [24,25]. During the performance of CALYPSO, various supercell sizes range from 1 to 4 formula units. The population size and the number of generations are 50 and 30, respectively. Initial random structures are generated by creating atomic coordinates through crystallographic symmetry operations, and 60% of the best structures are selected through the particle swarm optimization technique to construct the next generation. The underlying *ab initio* structural relaxations and electronic band structure calculations are carried out in the framework of the density functional theory (DFT) within generalized-gradient approximations using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and projector augmented wave (PAW) potentials [26,27] as played in the VASP code [28]. The structural relaxations are performed until the Hellmann-Feynman force on each atom reduces by less than 0.001 eV/Å. To ensure high accuracy, the $k$-point density and the plane waves cutoff energy are increased until the change of the total energy is less than $10^{-5}$ eV, and finally the Brillouin zone (BZ) integration is carried out using a $15 \times 15 \times 1$ Monkhorst-Pack grid in the first BZ. Plane waves with the kinetic energy up to 600 eV are employed. Additionally, the simulations are performed using a $2 \times 2 \times 1$ supercell based on a unit cell, and the repeated layered geometry is with a thick vacuum region of 20 Å.

**Results and discussions.**—The four most energetically favorable ones among the predicted structures are discussed here. Their total energies are listed in table 1, and the corresponding optimized geometries are plotted in fig. 1. The table shows that Struc1 has the lowest total energy with a value of at least 2.18 eV per primitive cell lower than those of the other structures, indicating by Struc1 the ground-state structure for SiBCN. The result can be clearly explained by the arrangement of the composed atoms. From fig. 1, it can be concluded that no Si-B or C-N bonds are formed in Struc1, which is very different from the other structures. According to the electronegativity of the four elements, the formation energies of Si-B and C-N bonds are higher than the other types of bonds, leading Struc1 to have the lowest total energy. In detail, fig. 1(a) clearly shows that every atom in Struc1 is bonded

| Struc1 | Struc2 | Struc3 | Struc4 |
|--------|--------|--------|--------|
| 0      | 2.18   | 3.24   | 3.38   |

Fig. 1: (Color online) The top and side views of the four energetically favorable structures of SiBCN. The blue, green, brown, and gray spheres present Si, B, C, and N atoms, respectively.
Graphene-like quaternary compound SiBCN etc.

Table 2: The bond lengths (in Å) in Struc1 SiBCN and the corresponding binary compounds given by experiment and our calculations.

|       | Si-C | Si-N | B-C | B-N |
|-------|------|------|-----|-----|
| SiBCN | 1.75 | 1.73 | 1.52| 1.50|
| SiC   | 1.89 [29] | – | – | – |
|       | (exp/cal) /1.89 | – | – | – |
| Si3N4 | – | 1.72 [30] | – | – |
|       | (exp/cal) /1.73 | – | – | – |
| B4C   | – | – | 1.43 [31] | – |
|       | (exp/cal) /1.44 | – | – | – |
| h-BN  | – | – | – | 1.44 [32] |
|       | (exp/cal) /1.44 | – | – | – |

by other two atoms and a graphene-like single-atom-thick structure is formed. The lengths of Si-C, Si-N, B-C, B-N bonds are 1.75, 1.73, 1.52, 1.50 Å, respectively. In order to compare with this configuration, the structural properties of the corresponding binary compounds SiC, Si3N4, B4C, and h-BN are calculated as well, and the calculated bond lengths agree well with the experimental ones, as listed in table 2. It is clear from the table that the Si-C bond length in Struc1 is shorter than 1.89 Å in bulk SiC [29], and the Si-N bond length is consistent with 1.72 Å in bulk Si3N4 [30], while the lengths of B-C and B-N bonds are much larger than 1.43 and 1.44 Å in B4C [31] and h-BN [32], respectively. The shortening of Si-C bond in SiBCN compared with that in bulk SiC can be explained by the fact that the radii of B and N atoms are much shorter than that of Si, thus replacing Si with B and N atoms would induce the compression of SiC volume, resulting in the shortening of the Si-C bond. For the lengths of B-C and B-N bonds, the situation is just the contrary. The lengths of Si-C, Si-N bonds decrease from 1.75 to 1.73 Å, caused by the shortening of the atomic radius from C to N. This rule can also explain the fact that the length of the B-N bond is shorter than that of the B-C bond. The difference of bond lengths causes the slight deformation of hexagonal structure. From the side view, Struc1 displays an absolutely flat structure, namely no buckling is built. This is attributed to the no formation of the Si-Si bond.

Owing to the result that Struc1 is the ground-state structure of SiBCN, the thermodynamic stability of this SiBCN structure is discussed through the cohesive energy. The cohesive energy is defined as follows:

\[ \Delta E = \frac{(2E_{Si} + 2E_B + 2E_C + 2E_N - E_{SiBCN})}{8}, \]

where \( E_{SiBCN} \) is the total energy of one SiBCN primitive cell, \( E_{Si}, E_B, E_C \) and \( E_N \) are the total energies of the isolated single Si, B, C and N atoms, respectively. The calculated cohesive energies, including those of graphene, h-BN, and silicene for comparison, are listed in table 3. The cohesive energy of SiBCN is 6.35 eV per atom. This value is a bit lower than those of graphene and h-BN, but is much higher than that of silicon. This is consistent with the fact that graphene and h-BN can be freestanding, while silicon must be grown on some matched substrates. The relatively high cohesive energy of SiBCN demonstrates that the graphene-like structure could exist stably.

To further evaluate the thermal stability of SiBCN, the \textit{ab initio} molecular dynamics (AIMD) simulations were performed. During the calculations, a large 4 × 4 × 1 supercell based on a primitive cell is employed, AIMD simulations are calculated using the NVT ensembles, the temperature controlled by the Nosé-Hoover method ranges from 300 K to 2000 K, and the simulations last for 10 ps with a time step of 2.0 fs. Simulation snapshots of the last step for SiBCN at different temperature are described in fig. 2. From the top and side views, it clearly shows that there is no breaking of the bonds and the original configuration is well kept even at the high temperature of 2000 K. Such high thermal stability of single-atom-layer SiBCN maybe is originated from the the high thermal stability of the metastable amorphous bulk SiBCN [21, 22]. The above performance means that the single-atom-layer SiBCN possesses high thermal stability, indicating their potential applications even at extremely high temperature.
Fig. 3: (Color online) (a) The density of electronic states (DOS) and (b) partial density of electronic states (PDOS) of Struc1 SiBCN. (c) The band structure of Struc1 SiBCN using PBE (black line) and HSE (red line) functionals. (d) The projected density of electronic states B, C, N, and Si, respectively.

Encouraged by the stability of SiBCN, the electronic property of this new single-atom-thick material is uncovered furthermore. The density of electronic states (DOS) and partial density of electronic states (PDOS) are described in figs. 3(a) and (b). The DOS clearly shows that the SiBCN behaves as semiconductor with a wide energy gap of \( \sim 2.63 \text{ eV} \) which is just between 2.20 and 3.39 eV for SiC and GaN, respectively [33]. Usually, the PBE functional would underestimate the band gap, the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE), which can usually give more accurate band gaps than that of the PBE functional, is employed additionally. The calculated band gap is \( \sim 3.50 \text{ eV} \). This indicates that SiBCN can be a potential candidate to be utilized in the corresponding fields of SiC and GaN applied. The PDOS presents that the valence band is mainly composed of C 2p states and some of N 2p states, while the conduction band is mainly composed of B 2p and Si 3p states and some of N 2p states. In the energy range below \( E_F \), there are many PDOS peaks of the four elements located at the same energy levels. This performance demonstrates that there are strong interactions among the neighboring atoms, which is confirmed by the electron localization functions (ELF) described in fig. 4. A high ELF indicates that it is likely probable to find a second electron with the same spin in the neighboring region of the referred one, i.e., the referred electron is highly localized [34]. The figure clearly shows that the strong bonds are formed between the nearest neighboring atoms, and all the bonds have \( \sigma \) characteristic. The formation of strong bonds can well explain why the compound still keeps the original structure even at extremely high temperature.

Since semiconductors with a direct band gap are more suitable for the applications, the band structure of SiBCN is explored next. The band dispersion curves are plotted in fig. 3(c). From the figure, it can be clearly concluded that the valence band maximum (VBM) and the conduction band minimum (CBM) are situated at the same reciprocal point \( B \). This elucidates that SiBCN is a direct band gap semiconductor. Additionally, fig. 3(d) also shows that the valence band is mainly composed of C and N 2p\(_z\) states and the conduction band is mainly composed of B 2p\(_z\) and Si 3p\(_z\) states, respectively. This characteristic can be confirmed by the partial (band decomposed) charge density of valence and conduction band edges, as plotted in fig. 5. The figure shows that the charges are mainly located on C atoms in the valence band, and they are mainly situated on Si and B atoms in the conduction band, illustrating that there exists different delocalization between the two band edges. It is caused by the different composition in valence and conduction band edges, which can be concluded from fig. 3. The valence band edge is mostly composed of C orbitals and minimally of N orbitals. For the conduction band edge, the majority is composed of Si and B states, and the minority is composed of N state. This results in the fact that the partial charge density of the valence band edge is mainly located on the C site, while...
that of the conduction band edge prefers expanding along the $B$-$K$ direction.

Finally, the carrier effective mass is evaluated due to its importance for the practical application of semiconductors. Here the electron effective mass ($m^*_e$) at CBM and hole effective mass ($m^*_h$) at VBM are defined by the following expression:

$$m^* = \frac{h^2}{E} \frac{\partial^2 E}{\partial k^2}^{-1},$$

where $E$ and $k$ are the energy and reciprocal lattice vector along the monolayer. The calculated $m^*_e$ is 3.79 and 0.45 $m_0$ along the $B$-$\Gamma$ and $B$-$K$ directions, respectively, and the $m^*_h$ is 1.48 and 0.33 $m_0$ along the two directions ($m_0$ denotes the free-electron mass). It is clear that both $m^*_e$ and $m^*_h$ along the $B$-$\Gamma$ direction are much heavier than the ones along the $B$-$K$ direction. This carrier effective mass anisotropy can be explained by the partial charge density of valence and conduction band edges in fig. 5. The figure indicates that the charge prefers expanding along the $B$-$K$ direction rather than along $B$-$\Gamma$ direction, telling that the carrier transport along the $B$-$K$ direction is easier than along the $B$-$\Gamma$ direction. A small effective mass usually represents high carrier mobility, this encourages us to explore the charge carrier transport property furthermore. The phonon limited carrier mobility in 2D materials can be calculated by the definition [35–39]

$$\mu_{2D} = \frac{e \hbar^2 C_{2D}}{k_B T m^* m_a (E_l)^2},$$

where $e$ is the electron charge, $\hbar$ is Planck’s constant divided by $2\pi$, $k_B$ is Boltzmann’s constant, $T$ is the temperature and 300 K is employed here. $m^*$ is the effective mass in the transport direction, and $m_a$ is the average effective mass determined by $m_a = (m^*_{B\Gamma} m^*_{BK})^{1/2}$. $C_{2D}$ is the elastic modulus of the longitudinal strain in the propagation directions of the longitudinal acoustic wave and is defined by $(E - E_0)/S_0 = C_{2D} (\Delta l/l_0)^2/2$, here $E$ is the total energy and $S_0$ is the lattice volume at equilibrium for a 2D system. $E_l$ represents the deformation potential constant of VBM for hole or CBM for electron along the transport direction and is expressed by $E_l = \Delta V_i/\Delta l/l_0$, where $\Delta V_i$ is the energy change of the $i$-th band under proper cell compression and dilatation, $l_0$ and $\Delta l$ are the lattice constant in the transport direction and the deformation of $l_0$, respectively. According to this equation, the evaluated electron mobility is $\sim 5.14\times 10^3$ cm$^2$/V·s$^{-1}$ along the $B$-$K$ direction and $\sim 0.61\times 10^3$ cm$^2$/V·s$^{-1}$ along the $B$-$\Gamma$ direction, the hole mobility is calculated as $\sim 13.07\times 10^3$ cm$^2$/V·s$^{-1}$ along the $B$-$K$ direction and $\sim 2.91\times 10^3$ cm$^2$/V·s$^{-1}$ along the $B$-$\Gamma$ direction, respectively. This mobility is much higher than $\sim 58.80$ cm$^2$/V·s$^{-1}$ of boron nitride nanoribbons [40] and $\sim 0.3$ cm$^2$/V·s$^{-1}$ of MoS$_2$ [41], and is of the same order of magnitude as $\sim 10^3$ cm$^2$/V·s$^{-1}$ of atomically thin InSe [18]. High carrier mobility indicates that SiBCN could be a suitable material for high efficiency solar cells.

**Conclusions.** – In conclusion, a new wide direct band gap semiconductor, SiBCN, is predicted by using first-principles calculations in combination with a swarm structure search method. The results show that SiBCN has a graphene-like structure and every atom is bonded with the other types of atoms, and this atomic configuration can be kept even at extremely high temperature. Further investigation also tells that SiBCN exhibits high carrier mobility. Since it has a wide direct band gap and high carrier mobility, SiBCN can be utilized in modern industry, such as integrated circuit, power component, etc.

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REFERENCES

[1] Boon K. T. and Sun X. H., Chem. Rev., 107 (2007) 1454.
[2] Tang Q. and Zhou Z., Prog. Mater. Sci., 58 (2013) 1244.
[3] Rao C. N. R., Gopalakrishnan K. and Maitra U., Appl. Mater. Interfaces, 7 (2015) 7899.
[4] Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V. and Firsov A. A., Science, 306 (2004) 666.
[5] Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Katsnelson M. I., Grigorieva I. V., Dubonos S. V. and Firsov A. A., Nature, 438 (2005) 197.
[6] Pacilé D., Meyer J. C., Girit Ç., Ö. and Zettl A., Appl. Phys. Lett., 92 (2008) 133107.
[7] Andrew J. M., Zhou X. F., Kiraly B., Wood J. D., Alducin D., Myers B. D., Liu X. L., Fisher B. L., Santiago U., Guest J. R., Yacaman M. J., Ponce A., Oganov A. R., Hersam M. C. and Guisan N. P., Science, 3267 (2015) 1513.
[8] Cahangirov S., Topakal M., Aktürk E., Sahin H. and Ciraci S., Phys. Rev. Lett., 102 (2009) 236804.
[9] Ding Y. and Ni J., Appl. Phys. Lett., 95 (2009) 083115.
[10] Liu H., Neal A. T., Zhu Z., Luo Z., Xu X. F., Tománek D. and Ye P. D., ACS Nano, 8 (2014) 4033.
[11] Xu M. S., Liang T., Shi M. M. and Chen H. Z., Chem. Rev., 113 (2013) 3766.
[12] Chen L., Liu C. C., Feng B. J., He X. Y., Cheng P., Ding Z. J., Meng S., Yao Y. G. and Wu K. H., Phys. Rev. Lett., 109 (2012) 056804.
[13] Wu H. P., Qian Y., Lu R. F. and Tan W. S., Phys. Lett. A, 380 (2016) 768.
[14] Wu F., Huang C. X., Wu H. P., Lee C., Deng K. M., Kan E. J. and Jena P., Nano Lett., 15 (2015) 8277.
[15] Rubio A., Corkill J. L. and Cohen M. L., Phys. Rev. B, 49 (1994) 5081.
[16] Mak K. F., Lee C. G., Heinz T. F., Phys. Rev. Lett., 105 (2010) 136805.
[17] Tran V., Sokolaski R., Liang Y. F. and Yang L., Phys. Rev. B, 89 (2014) 235319.
[18] Bandurin D. A., Tyurnina A. V., Yu G. L., Mishchenko A., Zolyomi V., Morozov S. V.
Kumar R. K., Gorbachev R. V., Kudrynskyi Z. R., Pezzini S., Kovalyuk Z. D., Zeitler U., Novoselov K. S., Patanè A., Eaves L., Grigorieva I. V., Fal’ko V. I., Geim A. K. and Cao Y., Nat. Nanotechnol., 12 (2017) 223.

[19] Du Y., Zhuang I. C., Liu H. S., Xu X., Eilers S., Wu K. H., Cheng P., Zhao J. J., Pi X. D., See K. W., Peleckis G., Wang X. L. and Dou S. X., ACS Nano, 8 (2014) 10019.

[20] Ni Z. Y., Liu Q. H., Tang K. C., Zheng J. X., Zhou J., Qin R., Gao Z. X., Yu D. P. and Lu J., Nano Lett., 12 (2012) 113.

[21] Kong J., Wang M. J., Zou J. H. and An L. N., Appl. Mater. Interfaces, 7 (2015) 6733.

[22] Widgeon S., Mera G., Gao Y., Sen S., Navrotsky A. and Riedel R., J. Am. Ceram. Soc., 96 (2013) 1651.

[23] Zhang M., Gao G. Y., Kutana A., Wang Y. C., Zou X. L., Tse J. S., Yakobson B. I., Li H. D., Liu H. Y. and Ma Y. M., Nanoscale, 7 (2015) 12023.

[24] Wang Y., Lv J., Zhu L. and Ma Y. M., Phys. Rev. B, 82 (2010) 094116.

[25] Wang Y., Lv J., Zhu L. and Ma Y. M., Comput. Phys. Commun., 183 (2012) 2063.

[26] Perdew J. P., Burke K. and Ernzerhof M., Phys. Rev. Lett., 77 (1996) 3865.

[27] Kresse G. and Joubert D., Phys. Rev. B, 59 (1999) 1758.

[28] Kresse G. and Furthmüller J., Comput. Mater. Sci., 6 (1996) 15.

[29] Mesquita A. H., Acta Crystallogr., 23 (1967) 610.

[30] Hardie D. and Jack K. H., Nature, 180 (1957) 332.

[31] Larson A. C., AIP Conf. Proc., 140 (1986) 109.

[32] Jin C. H., Lin F., Suehira K. and Iijima S., Phys. Rev. Lett., 102 (2009) 195505.

[33] Morkoç H., Strite S., Gao G. B., Lin M. E., Sverdlov B. and Burns M., J. Appl. Phys., 76 (1994) 1363.

[34] Becke A. D. and Edgecombe K. E., J. Chem. Phys., 92 (1990) 5397.

[35] Bruzzone S. and Fiori G., Appl. Phys. Lett., 99 (2011) 222108.

[36] Takagi S.-I., Toriumi A., Iwase M. and Tango H., IEEE Trans. Electron Dev., 41 (1994) 2357.

[37] Fiori G., Proc. IEEE, 101 (2013) 1653.

[38] Qiao J., Kong X., Hu Z.-X., Yang F. and Ji W., Nat. Commun., 5 (2014) 4475.

[39] Xie J. F., Zhang Z. Y., Yang D. Z., Xue D. S. and Si M. S., J. Phys. Chem. Lett., 5 (2014) 4073.

[40] Zeng H., Zhi C., Zhang Z., Wei X., Wang X., Guo W., Bando Y. and Golberg D., Nano Lett., 10 (2010) 5049.

[41] Novoselov K. S., Jiang D., Schedin F., Booth T. J., Khotkevich V. V., Morozov S. V. and Geim A. K., Proc. Natl. Acad. Sci. U.S.A., 102 (2005) 10451.