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### 1 Introduction

III-Nitrides and their multicomponent alloys have led to significant progress in the semiconductor industry, particularly in light-emitting diodes (LED),<sup>1,2</sup> laser diodes,<sup>3</sup> photodetectors (PDs),<sup>4,5</sup> and high-power/high-frequency electronics.<sup>6</sup> The incorporation of IIIA group metal elements (including aluminium, gallium, and indium) has been frequently used to tune the properties of materials, such as the bandgap, refractive index, and polarization.<sup>7–13</sup> Replacing the cation with boron, the lightest element of the IIIA group, can also increase the flexibility of applications.<sup>14–17</sup> The B<sub>x</sub>Al<sub>1-x</sub>N/AlN superlattice would enable a high density of two-dimensional electron gas (2DEG) in its layers<sup>14</sup> since wurtzite boron nitride (w-BN) possesses the strongest spontaneous polarization of 2.174 C m<sup>-2</sup> (ref. 18 and 19) in III-nitrides. Besides, effective refractive

## Morphology and carrier mobility of high-Bcontent $B_xAl_{1-x}N$ ternary alloys from an *ab initio* global search<sup>†</sup>

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The excellent properties of III-nitrides and their alloys have led to significant applications in optoelectronic devices. Boron, the lightest IIIA group element, makes it possible to extend the flexibility of III-nitride alloys. However, both  $B_xAl_{1-x}N$  and  $B_xGa_{1-x}N$  ternary alloys suffer from poor material quality during crystal growth, their B contents in experimental reports are no higher than 22%, and the underlying mechanism is still unclear. Herein, *ab initio* global calculation by particle swarm optimization combined with density functional theory is carried out to identify the ground structures of  $B_xAl_{1-x}N$  alloys with different B contents (x = 0.25, 0.5, and 0.75). Furthermore, the electronic properties and intrinsic carrier mobility are studied. For  $B_{0.25}Al_{0.75}N$  and  $B_{0.75}Al_{0.25}N$ , quasi-wurtzite and quasi-hexagonal structures are energetically favourable, respectively, indicating a wurtzite-to-hexagonal structural transition due to the three-co-ordinated B atoms being incorporated into the lattice. When the B content is 50%,  $B_{0.5}Al_{0.5}N$  shows a tenmembered ring structure with an indirect bandgap of 3.52 eV and strong anisotropy of mobility. Our results uncover the mechanism of the structural and electronic property evolution with B content and pave a route for the application of B-containing III-nitride alloys.

index modification by minor boron incorporation is observed in experiments, which makes  $B_xAl_{1-x}N$  suitable for highly refractive distributed Bragg reflectors (DBRs).<sup>15,16</sup> Undoped  $B_xAl_{1-x}N$  can also replace the conventional  $Al_{1-x}Ga_xN$  in the electron-blocking layer (EBL) in LEDs, which suffers from p-doping problems.<sup>17</sup> However, there are the following two difficulties in alloying boron compared with other III-nitrides:

(1) The poor quality of the materials. Significant phase separation has been frequently observed for  $B_xAl_{1-x}N$  or  $B_rGa_{1-r}N$ .<sup>20-22</sup> Two main factors should be attributed to this. Firstly, the ground states of BN and other III-nitrides are different: hexagonal for BN and wurtzite for other III-nitrides, indicating that B prefers planar three-coordination while other IIIA metal elements prefer tetrahedral four-coordination in nitrides. Secondly, the length of the B-N bonds is much smaller than that in IIIA metal nitrides; thus, the B substitution induces serious local distortion, which leads to the kinetic instability of the alloy lattice, particularly for high B content materials. This has been confirmed by experimental studies, in which high-B-content  $B_xAl_{1-x}N$  or  $B_xGa_{1-x}N$  alloys were quite hard to prepare by either metal-organic chemical vapor deposition (MOCVD)<sup>22-26</sup> or molecular beam epitaxy (MBE).<sup>27,28</sup> Usually, the B contents are below 15% (ref. 23 and 24) but reach 22% for wurtzite  $B_xAl_{1-x}N$ .<sup>25</sup> The B contents are typically less than 5% for wurtzite  $B_xGa_{1-x}N$ .<sup>26,28</sup>



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#### Paper

(2) How B affects the electronic properties of the alloys is still unclear. The bandgap of BN is identified to be indirect,<sup>29</sup> but other III-nitrides are direct bandgap semiconductors.<sup>30-34</sup> Therefore, B may change the optical properties of the alloys;<sup>35-37</sup> however, few reports focus on this. Moreover, the morphological uncertainty induced by B also brings difficulties in investigating the properties of the alloys. Most reports have hypothesized wurtzite or hexagonal structures as the ground states to study the properties.<sup>38-42</sup> For instance, the electron properties and band bowing effect including the indirect-direct band transition above 28% B content of  $B_xAl_{1-x}N$  on wurtzite have been reported on tetrahedrally coordinated B-N structures.38 Piezoelectric polarization of wurtzite B<sub>x</sub>Al<sub>1-x</sub>N turned zero at around 87% B content.<sup>39</sup> Besides, the  $B_xAl_{1-x}N$  and  $B_xGa_{1-x}N$  structural stability and miscibility between the hexagonal and wurtzite structures were studied by taking substrate lattice constraints into account.<sup>40-42</sup> Indeed, a lack of evidence supports this hypothesis; the atomic configuration is pretty complex in reality, particularly for these structures with high B contents. The columnar polycrystalline feature was found through high-resolution transmission electron microscopy (HRTEM) for  $B_xAl_{1-x}N$  film<sup>22,43,44</sup> and crystal twinning was found when the B/III gas-flow ratios were more than 0.15.23 The TEM measurement of wurtzite-structured B<sub>0.22</sub>Al<sub>0.78</sub>N on AlN substrate was reported with 60-degree twinning crystal formation and 5 nm layer width above the substrate.25

In this work, we adopted  $B_xAl_{1-x}N$  (x = 0.25, 0.50, and 0.75) as an example to systematically investigate the structural and electronic property evolution by global structure search combined with first-principles calculations. The lattice kinetic stability of the ground states under various B contents was confirmed by phonon calculations. An increased structural anisotropy was demonstrated with increasing B content. The direct bandgap of AlN transited into an indirect bandgap in  $B_xAl_{1-x}N$  after the introduction of B atoms since the contributions of the band-edge states were changed. The carrier mobilities from 100 K to 400 K were predicted by resolving the linearized Boltzmann transport equation (BTE). Furthermore, we identified a new polymorph of  $B_{0.5}Al_{0.5}N$  with the space group *Ccm2*<sub>1</sub>, which showed a ten-membered ring structure different from the traditional honeycomb *P*6<sub>3</sub>*mc* structure.

### 2. Computational details

Energetically favourable structures of  $B_xAl_{1-x}N$  with different B contents were searched through the Crystal structure Analysis by Particle Swarm Optimization (CALYPSO) software combined with density functional theory (DFT) calculations.<sup>45,46</sup> We set a 30-population size of 30 iterations for each B content, with at most 16 atoms in a unit cell for each B content, after careful testing, and the results are shown in Fig. S1 in the ESI.<sup>†</sup> To verify the reliability of our calculations, we tested these parameters on the  $B_{0.125}Al_{0.875}N$  system, as shown in Fig. S2.<sup>†</sup> The results agree with previous experimental observations.<sup>24,44</sup>

DFT calculations were carried out by the projector-augmentedwave potential (PAW)47,48 formalism implemented in the Vienna Ab Initio Simulation Package (VASP).49,50 The Al:  $3s^{2}3p^{1}$ , B:  $2s^{2}2p^{1}$ , and N:  $2s^{2}2p^{3}$  states were treated as valence electrons. The electron exchange and correlation potentials were described by the Perdew-Burke-Ernzerhof (PBE)<sup>51</sup> formed within the generalized gradient approximation (GGA). To accurately calculate the band structure, the Heyd-Scuseria-Ernzerhof (HSE)<sup>52,53</sup> method was used to describe the exchange and correlation parts. The mixing parameter was set to  $\alpha = 0.33$ , which has been used in previous reports.<sup>38,54</sup> We set an energy cutoff of 600 eV and a k-point mesh of  $2\pi \times$ 0.04  $\text{\AA}^{-1}$  for structural relaxation. The energy and force convergencies were  $10^{-6}$  eV and 0.01 eV Å<sup>-1</sup>, respectively. Phase transitions for different B contents were calculated using the climbing image modification in the nudged elastic band (CINEB) method 55,56 and we adopted 4 images in total on each reaction path. Phonon calculations were calculated by Phonopy<sup>57</sup> with the finite displacement approach.<sup>58</sup>

Intrinsic carrier mobility was calculated in the Electron-Phonon Wannier (EPW)<sup>59,60</sup> software distributed within the QUANTUM ESPRESSO<sup>61</sup> soft package. We set an energy cutoff of 80 Ry and used scalar relativistic norm-conserving Perdew-Zunger<sup>62</sup> parameterization of the local density approximation (LDA) to density functional theory. The  $2s^22p^63s^23p^1$  electrons of Al atoms, 2s<sup>2</sup>2p<sup>1</sup> electrons of B atoms, and 2s<sup>2</sup>2p<sup>3</sup> electrons of N atoms were accurately described. In this work, we calculated the carrier drift mobility of w-AlN, h-BN, B<sub>0.25</sub>Al<sub>0.75</sub>N, B<sub>0.5</sub>Al<sub>0.5</sub>N, and B<sub>0.75</sub>Al<sub>0.25</sub>N from 100 K to 400 K. Calculations of the carrier drift mobility were carried out under self-energy relaxation time approximation (SERTA)<sup>63</sup> by solving the Boltzmann transport equation. By considering both the driving force and scattering contributions, the iterative Boltzmann transport equation (BTE) mobility was calculated by self-consistent iterations. All electron-phonon scattering processes were considered. Details about the BTE equation are shown in ESI.†

### 3 Results and discussion

# 3.1 Global structure searching and structural evolution for stable $B_xAl_{1-x}N$ alloys

We have performed global structure searches at different B contents (x = 0.25, 0.50, and 0.75) for the  $B_xAl_{1-x}N$  alloy. The results of the free energy *versus* generations are shown in Fig. 1, and we especially zoomed in on the energy window 60 meV above the lowest energy to clarify the structural evolution with generations. The lattice stability of the ground states for each B content was confirmed by the calculated phonon spectrum, as shown in the ESI (Fig. S4†). The high B content alloy suffered serious phase separation. <sup>64–66</sup> Therefore, we adapted a 5 nm wide phase separation of the  $B_xAl_{1-x}N$  structures with different B concentrations to verify the stability of the searched ground structures. We find that the free energies for these phase separation structures are higher than that



Fig. 1 Energy evolution of the global structure search results *versus* generations of (a)–(c)  $B_{0.25}Al_{0.75}N$ ,  $B_{0.5}Al_{0.5}N$ , and  $B_{0.75}Al_{0.25}N$ , respectively. The energy windows 60 meV higher than the lowest energy structures are especially zoomed in. The atomic configurations of the ground states for each B content are shown in (d)–(f). 2 × 2 × 2 supercells are used, and the unit cells are marked by dashed boxes. The purple, green, and blue spheres represent Al, B, and N atoms.

for the searched ground structures by 16, 90, and 10 meV, respectively, indicating their lower thermodynamic stability, as shown in Fig. S3.† The details are discussed in the ESI.†

In  $B_{0.25}Al_{0.75}N$ , as shown in Fig. 1a, we found that most structures with low energy exhibited a *P*1 space group. Besides, the *P*6<sub>3</sub>*mc*, *I*42*m*, and *Cm* symmetries were included in the lowenergy scale. The atomic configuration of the ground state is shown in Fig. 1d. It was similar to the wurtzite structure (socalled quasi-wurtzite), in which the Al atoms remained in tetrahedral coordination like in the wurtzite structure, but the B atoms remained in planar coordination. The B–N bonds were stretched from 1.45 to 1.54 Å; therefore, the B atoms induced local stress on the materials. The wurtzite structure with the *P*6<sub>3</sub>*mc* space group also appeared with a higher energy than the ground state of 3 meV per atom (blue dot in Fig. 1a). Therefore, the B<sub>x</sub>Al<sub>1-x</sub>N alloy showed neither wurtzite nor hexagonal structure even at low B contents.

For  $B_{0.5}Al_{0.5}N$ , continuously found structures in the PSO structural relaxation through generations were verified with the *Ccm*2<sub>1</sub> space group, as shown in Fig. 1e. Notably, the ground state exhibited a unique stretched-hexagonal morphology perpendicular to the *c*-axis, which has not been reported before. The stretched-hexagon was composed of ten atoms, in which the Al and B atoms were still in tetrahedral and planar coordination, instead of a regular hexagon configuration like in the wurtzite structure. We also tested the free energy of wurtzite  $B_{0.5}Al_{0.5}N$ , which was 500 meV per atom higher than that for the searched ground state, indicating the increased lattice instability of the wurtzite structures for  $B_xAl_{1-x}N$  alloys with higher B contents.

By increasing the B content to 75% ( $B_{0.75}Al_{0.25}N$ ), we found that the ground state evolved into a quasi-hexagonal structure with the *P*1 space group (Fig. 1c) due to the B atoms becoming

the majority cations, which are vital to the atomic configuration. The quasi-hexagonal structure could be described as a distorted hexagonal BN connected by tetrahedral-coordinated Al atoms, as shown in Fig. 1f. We also artificially constructed wurtzite and hexagonal structures for B<sub>0.75</sub>Al<sub>0.25</sub>N, which after structural optimization, relaxed to the quasi-hexagonal structures, implying the significant instability of both structures.

By comparing the ground states at different B contents, we can find two trends: (1) the B and Al atoms prefer to keep their stable configurations (planar coordination for B and tetrahedral four coordination for Al), which leads to instability in the  $B_xAl_{1-x}N$  alloy lattices. Therefore, the  $B_xAl_{1-x}N$  alloys show serious phase separation instead of a stable solid solution, unlike the  $Al_xGa_{1-x}N$  alloys. (2) The atomic configurations undergo a phase transition from quasi-wurtzite to quasi-hexagonal structures. To understand these, we performed nudged elastic band (NEB) calculations for the ground states at different B contents, and the results are displayed in Fig. 2a-c. For  $B_{0.25}Al_{0.75}N$ , we set the searched ground structure as the initial state and the relaxed wurtzite structure as the final state, as shown in Fig. 2a. The NEB calculation showed a 0.92 eV barrier, which was much larger than  $k_{\rm B}T$  (0.03 eV at 299 K), and a 0.51 eV energy barrier in the reverse reaction path. Thus, the wurtzite structure was also a local minimum and could be stable. For B<sub>0.5</sub>Al<sub>0.5</sub>N, we also constructed the final structure by moving the B atoms of the searched ground structure from planar coordination to tetrahedral coordination. A free energy increase of 2.10 eV was obtained, as shown in Fig. 2b, indicating that the wurtzite lattice for B<sub>0.5</sub>Al<sub>0.5</sub>N was quite unstable even in a metastable state. This was also confirmed by the calculated phonon modes, as shown in Fig. 2d. We highlighted the vibration modes of the imaginary frequency around gamma with green arrows. It was observed that the wurtzite



**Fig. 2** Structural transitions for the ground states at different B contents in (a)  $B_{0.25}Al_{0.75}N$ , (b)  $B_{0.5}Al_{0.5}N$  and (c)  $B_{0.75}Al_{0.25}N$ . The insets are the initial, transition, and final structures. (d) The calculated phonon spectrum for  $B_{0.5}Al_{0.5}N$ ; the vibration mode for the imaginary frequency is highlighted by dashed box.

structure tended to reconstruct to the *Ccm*2<sub>1</sub> space group for  $B_{0.5}Al_{0.5}N$ . A similar result was obtained for  $B_{0.25}Al_{0.75}N$ , as shown in the ESI (Fig. S7†). For  $B_{0.75}Al_{0.25}N$ , we attempted to set the hexagonal structure as the final state; however, it was quite unstable since the planar coordination Al was energetically unfavourable. The in-plane twisted hexagonal  $B_{0.75}Al_{0.25}N$  structure is shown in Fig. 2c through the NEB path. The 0.63 eV barrier should be overcome by breaking the sp<sup>3</sup> Al–N bond and forming the sp<sup>2</sup> Al–N bond, as shown in Fig. 2c.

#### 3.2 Electron structure and carrier properties

We paid special attention to the representative structures with the lowest energy for further research; therefore, in the following part,  $P1(aB_{0.25}Al_{0.75}N,$  $Ccm2_1 (a) B_{0.5} Al_{0.5} N$ , and P1@B<sub>0.75</sub>Al<sub>0.25</sub>N were selected. The atom positions and lattice parameters of  $B_xAl_{1-x}N$  are shown in Table S1<sup>†</sup> and the calculated lattice parameters, bandgaps, and effective masses are shown in Table S2.† Our results were reliable enough when compared with experimental and other theoretical results.<sup>29-33</sup> We calculated the band structures of these searched ground structures of  $B_xAl_{1-x}N$ , as are shown in Fig. 3, and the band structures of wurtzite AlN (w-AlN), hexagonal AlN (h-AlN), wurtzite BN (w-BN), and hexagonal BN (h-BN) are shown in Fig. S5† as references. All the  $B_xAl_{1-x}N$  alloys showed indirect band structures with gaps of 5.48 eV for  $P1@B_{0.25}Al_{0.75}N$ , 3.52 eV for  $Ccm2_1 \textcircled{0}B_{0.5}Al_{0.5}N,$  and 4.31 eV for P1  $\textcircled{0}B_{0.75}Al_{0.25}N$  under the HSE level. We can find thus make two statements: (1) the bandgaps change from direct (w-AlN) to indirect due to the introduction of B atoms; (2) there is no dependence between the bandgap and the composition of B for the  $B_xAl_{1-x}N$  alloys. These are quite different from the case with  $In_xGa_{1-x}N$  and  $Al_xGa_{1-x}N$  alloys, and these differences are induced by the



Fig. 3 Band structures of  $P1@B_{0.25}Al_{0.75}N$ ,  $Ccm2_1@B_{0.5}Al_{0.5}N$ , and  $P1@B_{0.75}Al_{0.25}N$  obtained at the PBE (black solid lines) and HSE06 (red dashed lines) levels. The Fermi level is set to zero and the band-edges are highlighted by blue circles.

changes in band-edge contributions (as shown in Fig. S6<sup>†</sup>) and the structural transitions after the incorporation of B atoms into the AlN lattice. The N-s and N-p orbitals contributed to the conduction band minimum (CBM) and valence band maximum (VBM), respectively, for the direct bandgap of w-AlN. For the indirect bandgap of h-BN, the B-p and N-p orbitals contributed to the CBM and VBM, respectively. In the  $B_xAl_{1-x}N$  alloys, the VBM still originated from the N-p orbitals, but the contribution of the CBM was changed. At low B contents (P1@B<sub>0.25</sub>Al<sub>0.75</sub>N), the CBM was contributed by the hybridized orbital between the B-p bonding orbitals and N-p antibonding orbitals. By increasing the В content (Ccm2<sub>1</sub>@B<sub>0.5</sub>Al<sub>0.5</sub>N and P1@B<sub>0.75</sub>Al<sub>0.25</sub>N), the B-p bonding orbitals gradually dominated the CBM like that in h-BN due to the same planar coordination as h-BN. Therefore, the direct-toindirect bandgap transition was observed. In contrast, the

In<sub>x</sub>Ga<sub>1-x</sub>N and Al<sub>x</sub>Ga<sub>1-x</sub>N alloys were still in the wurtzite ground structures, and thus the width of the bandgap monotonously depended on the energy level of the cation-N orbitals, which could be tuned by the compositions because the energies of the Al–N, Ga–N, and In–N bonds were quite different. However, in the B<sub>x</sub>Al<sub>1-x</sub>N alloys, not only the bond energies but also the bond feature, sp<sup>3</sup> to sp<sup>2</sup>, was changed due to the structural transition, as we discussed before. Thus, the width of the bandgap could not be tuned by B content.

 $B_xAl_{1-x}N$  is highly expected to be useful when applied in the undoped electron-blocking layer (EBL) to overcome the p-doping problem in  $Al_xGa_{1-x}N$ .<sup>17</sup> Therefore, the carrier mobility is quite important to the performance. However, there is a lack of reports on this for  $B_xAl_{1-x}N$  alloys. As far as we know, the intrinsic hole and electron mobilities were as low as 14 cm<sup>2</sup> (V S)<sup>-1</sup> (ref. 67) at 290 K and 130 cm<sup>2</sup> (V S)<sup>-1</sup> at 300 K for w-AlN<sup>68</sup> and 18–12.4 cm<sup>2</sup> (V S)<sup>-1</sup> at 700–790 K (ref. 69) and 48 cm<sup>2</sup> (V S)<sup>-1</sup> at 800 K for h-BN.<sup>70</sup> Here, we calculated the drift mobility for the ground states with different B contents, and the values for intrinsic w-AlN and h-BN are still given as references. Both the SERTA and BTE methods with Wannier interpolation were employed to accurately calculate the mobility, and the temperature scanning was from 100 K to 400 K with an interval of 50 K. The reliability of our settings was tested by GaN, and the results were comparable with the experimental observation.71,72 The structural parameters obtained from OE and VASP and the Wannier spread parameters are shown in Tables S3 and S4.<sup>†</sup> The calculated mobilities are shown in Fig. 4. The BTE mobility was about 2 times that of SERTA in GaN, as reported.<sup>72</sup> In our work, the BTE electron and hole mobilities for w-AlN were around 2.18/2.42 times those of the SERTA results and 1.30/1.38 times those of h-BN. The typical ratio values for  $B_xAl_{1-x}N$  were 1.73/1.89 for

 $B_{0.25}Al_{0.25}N$ , 2.49/2.65 for  $B_{0.5}Al_{0.5}N$  and 1.77/1.44 for  $B_{0.75}Al_{0.25}N$ . Finally, we selected self-consistent BTE mobility results in the following discussions. The results for w-AlN (left column) were 36.67 cm<sup>2</sup> (V S)<sup>-1</sup> and 445.36 cm<sup>2</sup> (V S)<sup>-1</sup> for hole and electron, respectively, and for h-BN (right column), they were 41.29 cm<sup>2</sup> (V S)<sup>-1</sup> and 45.44 cm<sup>2</sup> (V S)<sup>-1</sup> for hole and electron, respectively, at 300 K, which agreed with previous reports. The comparison with the experimental results for h-BN at higher temperatures is shown in Fig. S8.†

Generally, the intrinsic mobility is monotonously reduced by increasing the temperature due to the scattering by the enhancement of phonons, and the same trends were observed in our calculations. From the middle column of Fig. 4, we can find the B atom was harmful to the mobilities of both electrons and holes by comparing it with w-AlN. The mobilities were insensitive to the B content. P1@B0.75Al0.25N and  $Ccm_{2}(B_{0.5}Al_{0.5}N \text{ showed the highest } (54.97 \text{ cm}^2 (V \text{ S})^{-1}) \text{ and }$ lowest (26.48 cm<sup>2</sup> (V S)<sup>-1</sup> at 300 K) electron mobilities, with only about 0.12-0.06 of that of intrinsic w-AlN, respectively. In contrast, Ccm21@B0.5Al0.5N and P1@B0.75Al0.25N showed the highest (18.31 cm<sup>2</sup> (V S)<sup>-1</sup>) and lowest (5.92 cm<sup>2</sup> (V S)<sup>-1</sup>) hole mobility at 300 K, which were around half that of intrinsic w-AlN. Thus, the mobility of electrons was reduced more than that of the holes by the introduction of B atoms, benefiting the application of EBL in LEDs. Moreover, we separately plotted the mobility along with different directions in Fig. S9.† We found obvious anisotropy for carrier mobility in  $Ccm2_1$  (a)  $B_{0.5}Al_{0.5}N$ . The carrier mobility along the z-direction was about two times higher than that along the x- and v-directions.

The effective mass is a decisive factor for the carrier mobility, and so we calculated the effective masses for the  $B_xAl_{1-x}N$ alloys, which are the second derivatives of the eigenvalues of



**Fig. 4** Electron and hole intrinsic drift mobilities of B<sub>x</sub>Al<sub>1-x</sub>N *versus* temperature. Electron and hole mobilities are averaged on three directions for both BTE and SERTA calculations.



**Fig. 5** (a) Average effective masses of  $B_xAl_{1-x}N$  as a function of B content. x = 0 and 1 refer to wurtzite AlN and hexagonal BN, respectively. (b) Intrinsic electron and hole mobilities at 300 K.

the CBM and VBM in reciprocal space, including those of intrinsic w-AlN and h-BN as references. We plotted the effective masses and carrier mobilities at 300 K, as shown in Fig. 5, and the detailed results are listed in Table S2.† We found that the electron effective masses fluctuated in the range of 0.34 to 1.19, while the hole effective masses sharply reduced from 7.48 (intrinsic w-AlN) to the range of 0.96 to 1.89. Here, we paid attention to the carrier effective masses for the searched ground states of the  $B_xAl_{1-x}N$  alloys and found that the tendency for the carrier effective mass corresponds to higher mobility. Therefore, the effective mass was the decisive factor for the carrier mobility for the  $B_xAl_{1-x}N$  alloys, and the structural transition did not induce serious phonon scattering to affect the mobility.

### 4. Conclusions

In summary, we investigated the morphological and electronic properties of  $B_xAl_{1-x}N$  alloys by combining PSO analysis with DFT calculations. Unlike previous reports, we found that the  $B_xAl_{1-x}N$  alloys were in neither wurtzite nor hexagonal structures, because the B and Al preferred planar three and tetrahedral four coordination, like that in intrinsic w-AlN and h-BN, respectively, which was confirmed by structural transition and phonon analysis. Quasi-wurtzite and quasi-hexagonal structures were identified for low and high B contents, respectively. Particularly, we revealed a new structure for  $B_{0.5}Al_{0.5}N$  with the *Ccm*2<sub>1</sub> space group. Moreover, we studied the electronic properties of the  $B_xAl_{1-x}N$  alloys. The incorporation of B resulted in a direct-to-indirect bandgap transition

due to the B-p orbitals contributing to the edge states. Furthermore, the electron mobility was sharply reduced, implying that the  $B_xAl_{1-x}N$  alloys could be used as an electronblocking layer in LEDs.

### Author contributions

D. L. and Z. S. conceived the idea and provided advice on this work. Z. Q. carried out the calculations. Z. Q. and Z. S. wrote the manuscript. H. Z., X. M., Y. Y., Y. J., K. J., and X. S. provided very useful comments. All authors participated in the discussions on the results.

### Conflicts of interest

There are no conflicts to declare.

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