The first principle calculation of improving p-type characteristics of BXAl1-xN

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The first principle calculation of improving p-type characteristics of $B_xAl_{1-x}N$

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Abstract

AlN is one of the third-generation semiconductor materials with wide application prospects due to its 6.2eV band gap. In the application of semiconductor deep ultraviolet lasers, progress is slow due to the difficulty in obtaining p-type AlN with good performance. In this paper, the commonly used Mg dopants are abandoned, and the research on BAlN alloys is replaced. The improvement of the p-type properties of AlN crystals by B composition is studied by first-principles calculations. The results show that the addition of B composition can significantly inhibit the intrinsic n-type performance of AlN, which is beneficial to the formation of p-type AlN. At the same time, it has been found that when the composition of B reaches 19.5%, the BAlN compound semiconductor changes from n-type characteristics to p-type characteristics.

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Introduction

AlN has the widest band gap (6.2eV) among the Group-III nitride semiconductors.

Therefore, AlN plays a significant role in the development of solid-state ultraviolet light sources for light-emitting diodes and laser diodes. For such applications, both conductive n-and p-type AlN materials are required. The n-type AlN can be achieved by using traditional doping techniques that exchange atoms with impurities of additional electrons, such as Si doping[1-3], but the p-type AlN remains a major challenge.

At present, the following factors restrict the conductivity of p-type AlN: limited solubility in related receptors, high activation energy of acceptors, and compensation for impurities and natural donor defects[4]. In general, the p-type doping of III-nitride semiconductors is achieved by substituting dopants for the primary atom, which have fewer valence electrons than the primary atom[5]. For example, p-type GaN can be reproduced by MOCVD, Mg doping and annealing[6]. The activation energy of Mg receptor in GaN is about 160 MeV, while that in AlN is about 500 MeV[7-10]. Recent reports on the preparation of p-type AlN by Mg doping show that these empty points in the impurity band have a very high activation energy of about 600 MeV and a low mobility[11], which makes Mg-doped AlN ineffective in practical applications[12,13]. The results show that the void concentration at room temperature is about $10^{10}cm^{-3}$ in Mg-doped AlN.

In order to obtain p-type AlN with better conductivity, the self-compensation effect of AlN needs to be solved first. It is assumed that the main reason for the self-compensation effect of AlN is that the electronegativity of the Al and N atoms are different. At the process of electron hybridization, the electrons of N atom cannot be well bound, which makes the electrons of N atom relatively free, thus causing serious self-compensation effect. By first-principles calculation, we try to prove that substitution of B atom (electronegativity higher than Al atom) for Al atom can effectively reduce the self-compensation effect of AlN, thus lowering the activation energy of holes.

Methodology

This paper uses the first principles to calculate[14,15,16] the band bowing of BAlN with different composition of B. In order to obtain data of low concentration B composition, the supercell structure is too large to be calculated. Therefore, using virtual crystal as the calculation model, very low B composition can be obtained

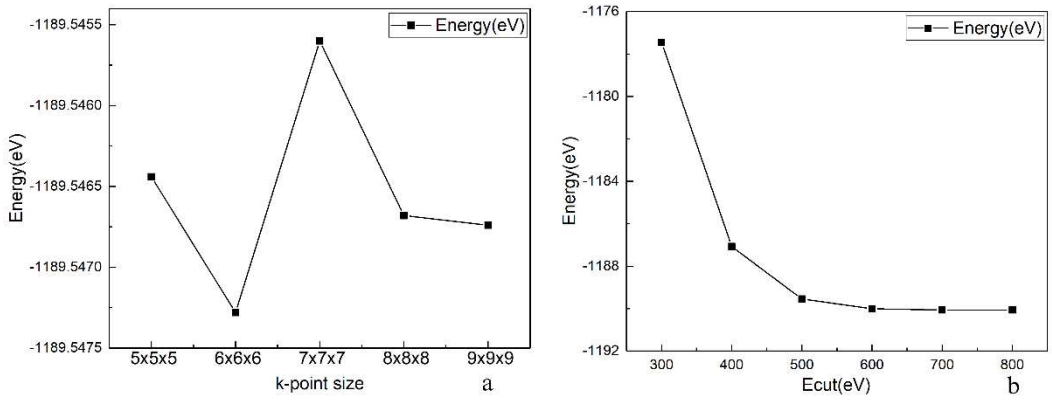

Fig. 1 K Point and Cut-off energy Test

without changing the periodicity of the crystal. With this method, the lattice constants and band structure of BAlN with different B composition are calculated. Among them, the valence electrons of Al atom are $3d^2 3p^1$, N atom is $2s^2 2p^3$, and B atom is $2s^2 2p^1$.

From Figure 1, it is possible that the energy calculation of the cell will vary with the selection of different K-point sizes and the Cut-off energy sizes. For a single cell, the lowest energy state is obtained when the Cut-off energy is 500 eV at 6 x 6 x 6 K-point size. The Cut-off energy tends to converge at 600eV while maintaining 6 x 6 x 6 K-point size. Although it is not in the lowest energy state, but the increase of Cut-off energy will increase the computational load of the computer, so using 600eV as the Cut-off energy can guarantee both low energy state and not giving too much load to the computer.

Table 1 Lattice optimization results

	GGA	LDA	HSE03	HSE06	Exp[17,18]
a(Å)	3.079	3.066	3.014	3.008	3.11
c(Å)	4.938	4.917	4.834	4.823	4.98

Different lattice optimization results for the original cell can be obtained by using different exchange-correlation potentials, as shown in Table 1. It can be seen that different exchange-correlation potentials can result in different optimized lattice constants, among which the GGA is the closest to the experimental values, so this algorithm is used in the crystal optimization process. After determining the optimization algorithm, comparing the band characteristics calculated for different exchange-correlation potentials yields results such as Table 2.

Table 2 calculation results of energy gap

	LDA	PBE	RPBE	PW91	BLYP	HSE06	Exp[18,19]
Eg(eV)	4.18	4.134	4.218	4.183	4.525	6.01	6.2

From Table 2, it can be seen that the optimal band gap can be obtained by the exchange-correlation potential of HSE06, but the algorithm cannot be used for the calculation of virtual crystals, so only the BLYP exchange-correlation potential closest to the experimental value can be selected as the calculation method of the band.

Results and Discussion

AlN and BN are both crystals with p63mc space group, but the BN of wurtzite is

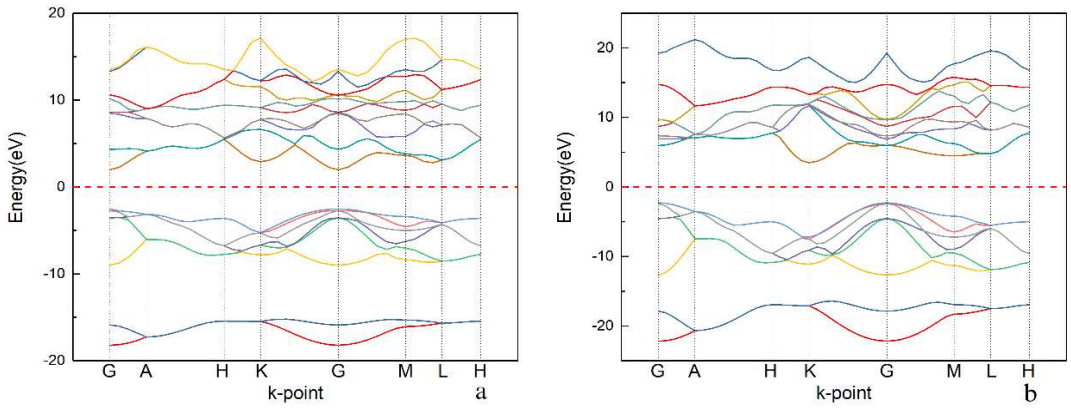

Fig. 2 Band structure of a) AlN, b) BN crystal

very unstable and difficult to obtain in the experiment, so the first principle is particularly important for its research. The two crystals have the same structure and can be studied as alloys. Because the electronegativity of B atom is 2.051, which is much larger than that of Al atom, if B atom is used to replace Al atom in AlN, a positive electric center will be formed, which is beneficial to improve the self-compensation

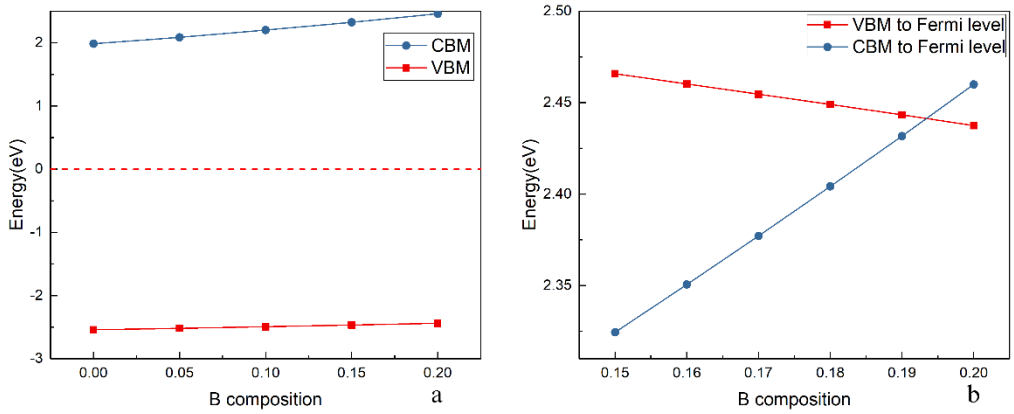

Fig. 3 Energy band of different B composition

effect of AlN and make p-type doping of AlN possible.

Firstly, the crystal band structures of AlN and BN with wurtzite structure are calculated. It can be seen that AlN crystal has a direct band gap (Figure 2a), and the Fermi energy level is in the middle of the conduction band and valence band, and is slightly close to the conduction band, showing n-type characteristics. BN crystal is an indirect band gap (Figure 2b), and the Fermi energy level is closer to the top of the valence band, which has a strong p-type property. Therefore, with the increase of B composition in $B_xAl_{1-x}N$ alloys, the transition from n-type semiconductor to p-type semiconductor and from direct band gap to indirect band gap will be formed.

Figure 3 can be obtained by calculating the position relationship between the top of the valence band and the bottom of conduction band when the value of x is from 0 to 0.2 with the interval of 0.05 for B composition by the method of virtual crystal. Figure 3a shows the position relationship between the top of the conduction band, the bottom of valence band and Fermi level for different B composition. In Figure 3b, the

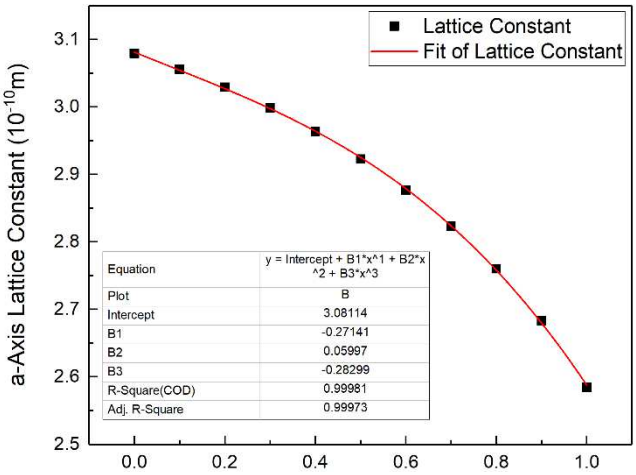

Fig. 4 lattice constant of a-Axis changing with B composition

solid line represents the energy difference between the bottom of the conduction band and the Fermi level; the dotted line represents the energy difference between the Fermi level and the top of the valence band. It can be seen from the figure that when composition of B is below 0.15, the difference between the valence band top and Fermi level of BAlN is still greater than that between the conduction band top and Fermi level, which shows the characteristics of n-type semiconductor. When the composition is increased to 0.2, the difference between the valence band top and Fermi level becomes smaller than that between the conduction band top and Fermi level, and the compound will show the characteristics of p-type semiconductor. It can be seen from the b-diagram that the B composition has completed the transition from n-type to p-type semiconductor near 19.5%. According to reference [20], B composition in BAlN compound is still a direct band gap semiconductor when it is lower than 28%.

Through the calculation of lattice optimization for different B composition virtual crystals, the change rule of lattice constant in a-Axis can be obtained, as shown in Figure 4. The formula for the change of lattice constant of a-Axis with the increase of B composition can be obtained by fitting:

$$a = 3.081 - 0.271x + 0.06x^2 - 0.283x^3$$

When the B composition is 20%, the lattice mismatch of AlN crystal and BAlN crystal is only 1.6%.

Conclusions

The electronegativity difference between Al atom and N atom may be too large in AlN crystal. During the formation of the crystal, the hybrid electrons of Al atom and N atom are not well bound in the hybrid process, showing certain free-electron characteristics. Therefore, there is a strong self-compensation characteristic in the process of Mg doping. Therefore, using B with higher electronegativity as a dopant can not only replace Al atom to form a positive center, but also increase the binding ability to electrons. It can be found that intrinsic BN has the properties of p-type semiconductor, while intrinsic AlN has the properties of n-type semiconductor. When the B composition reaches 19.5%, $B_xAl_{1-x}N$ changes from the properties of n-type semiconductor to the properties of p-type semiconductor. At the same time, it has been reported that when the B composition is less than 28%, the band gap of $B_xAl_{1-x}N$ is direct. When the a-axis lattice constant of the compound is calculated, it can be found that the lattice mismatch with AlN crystal is only 1.6% at 19.5% B composition. Therefore, the intrinsic n-type properties of AlN crystal can be effectively improved by using B as the doped materials, and even converted to p-type properties. This is very effective for the preparation of p-AlN crystal.

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Fig.1

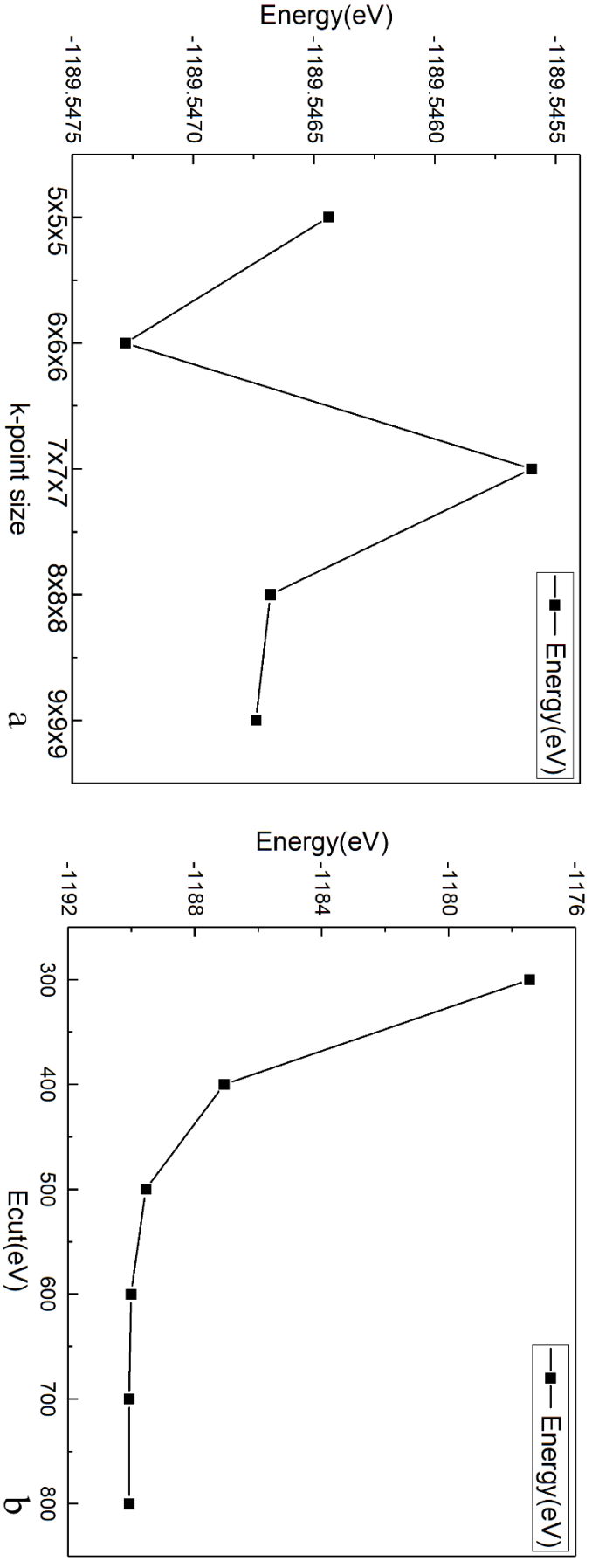
Energy(eV)
-1189.5455
-1189.5460
-1189.5465
-1189.5470
-1189.5475
5x5x5
6x6x6
7x7x7
8x8x8
9x9x9
k-point size
Energy(eV)
a
Energy(eV)
-1176
-1180
-1184
-1188
-1192
300
400
500
600
700
800
Ecut(eV)
Energy(eV)
b

Fig.2

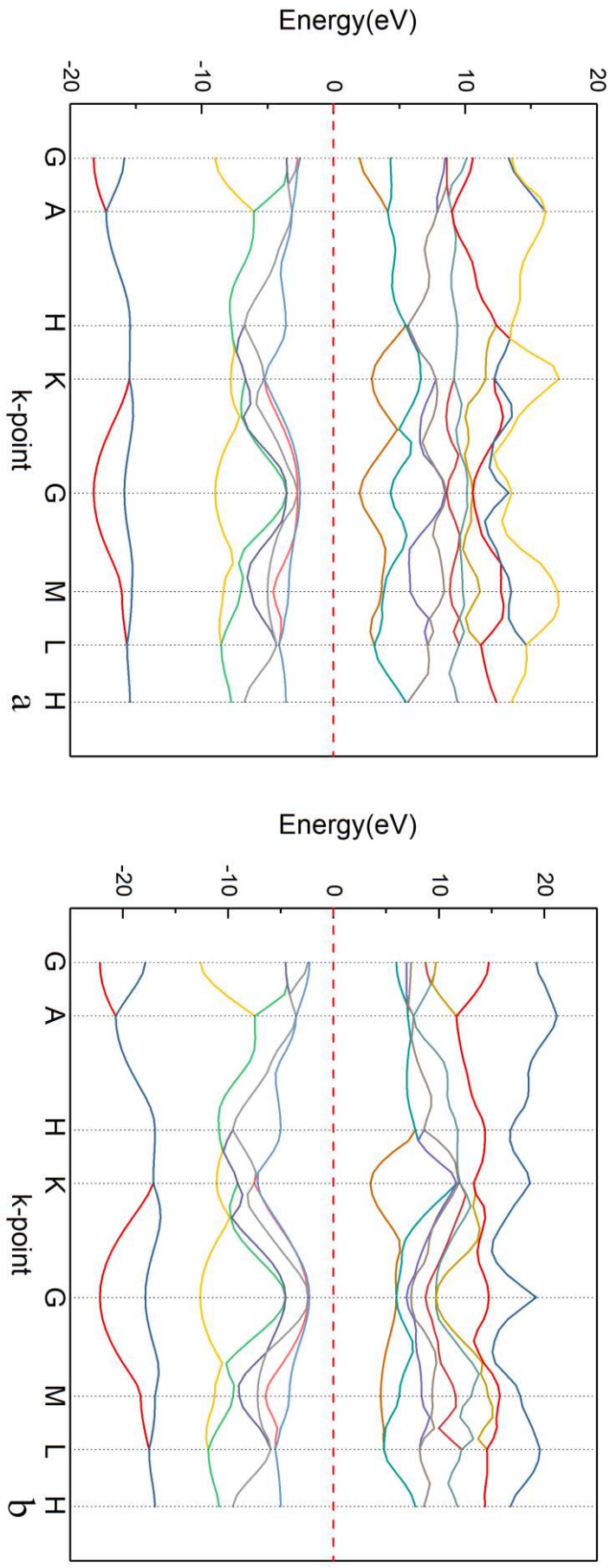
Energy(eV)
-20
-10
0
10
20
G
A
H
K
G
M
L
H
k-point
a
Energy(eV)
-20
-10
0
10
20
G
A
H
K
G
M
L
H
k-point
b

Fig.3

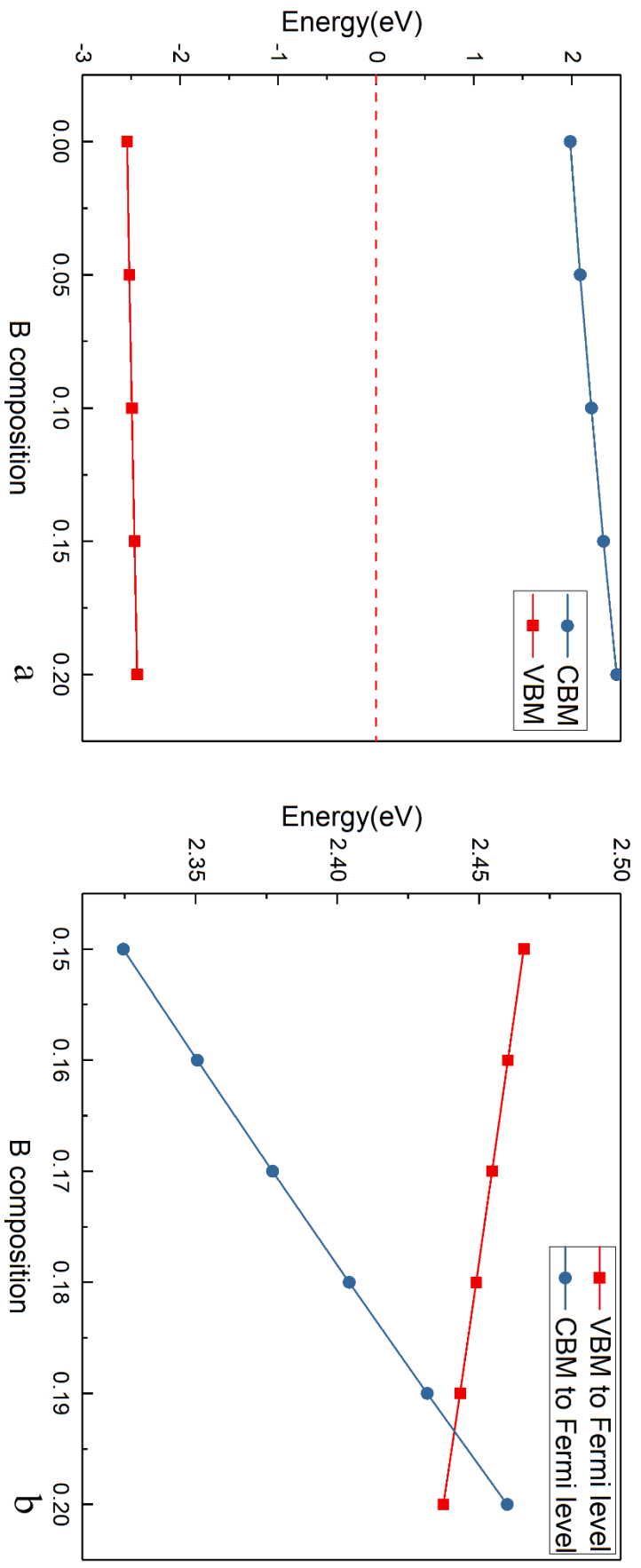
Energy(eV)
2
1
0
-1
-2
-3
0.00
0.05
0.10
0.15
0.20
B composition
a
CBM
VBM
Energy(eV)
2.50
2.45
2.40
2.35
0.15
0.16
0.17
0.18
0.19
0.20
B composition
b
VBM to Fermi level
CBM to Fermi level

Fig.4

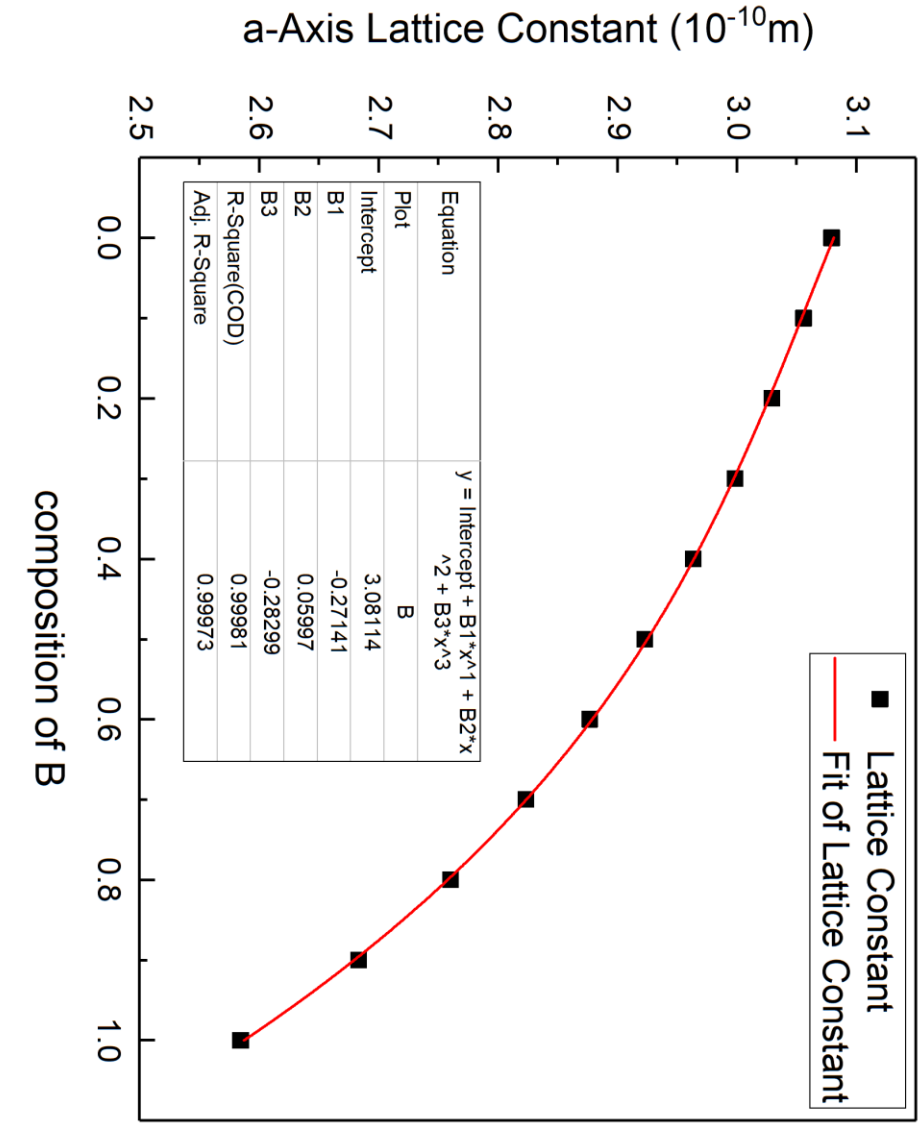
a-Axis Lattice Constant (10^-10m)
composition of B
Lattice Constant
Fit of Lattice Constant
Equation
y = Intercept + B1*x^1 + B2*x^2 + B3*x^3
Plot
B
Intercept
3.08114
B1
-0.27141
B2
0.05997
B3
-0.28299
R-Square(COD)
0.99981
Adj. R-Square
0.99973
2.5
2.6
2.7
2.8
2.9
3.0
3.1
0.0
0.2
0.4
0.6
0.8
1.0

Figure captions

Figures

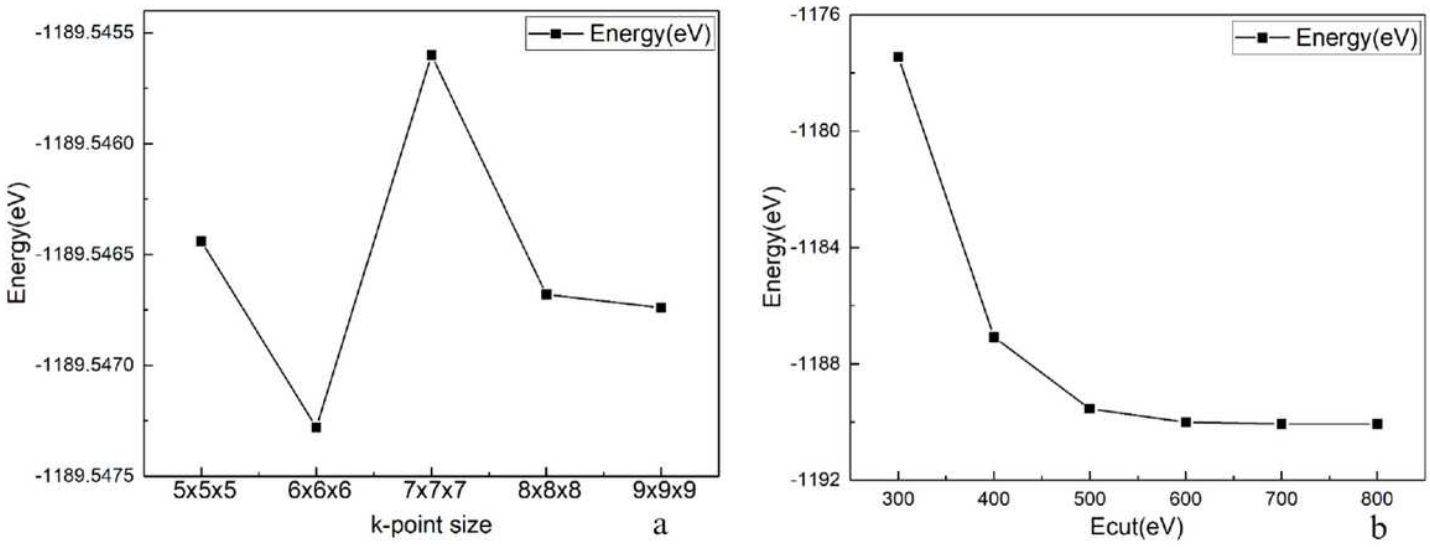

Figure 1

K Point and Cut-off energy Test

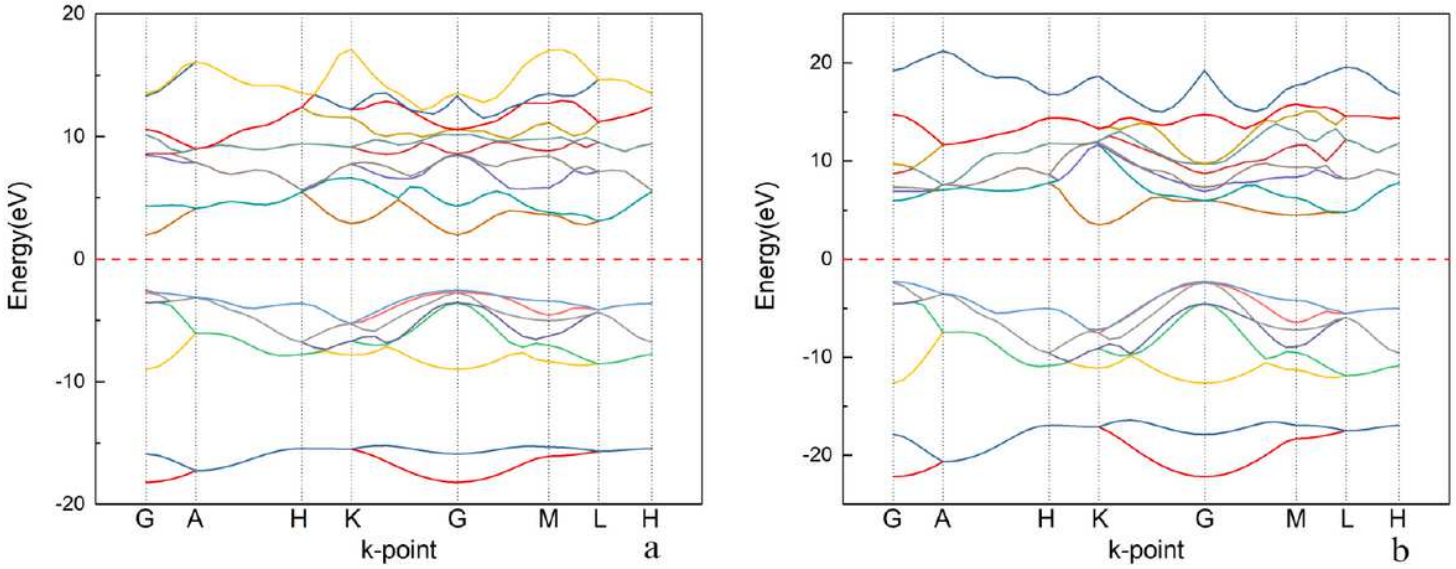

Figure 2

Band structure of a) AlN, b) BN crystal

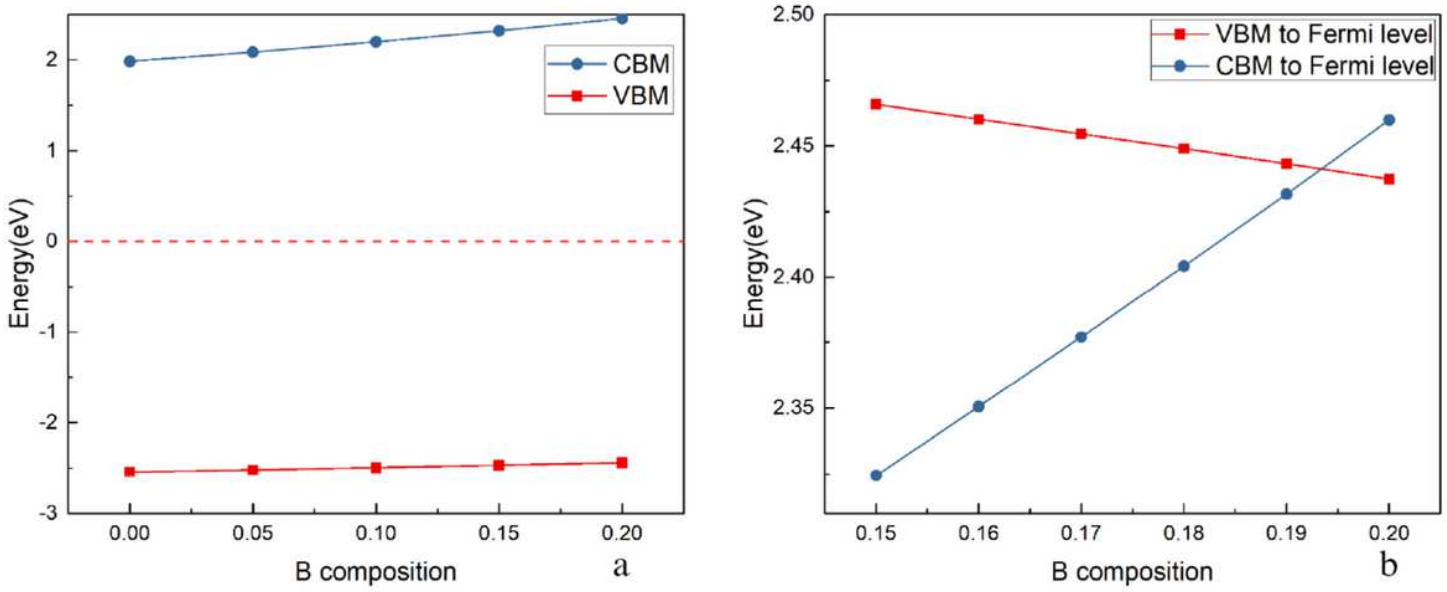

Figure 3

Energy band of different composition

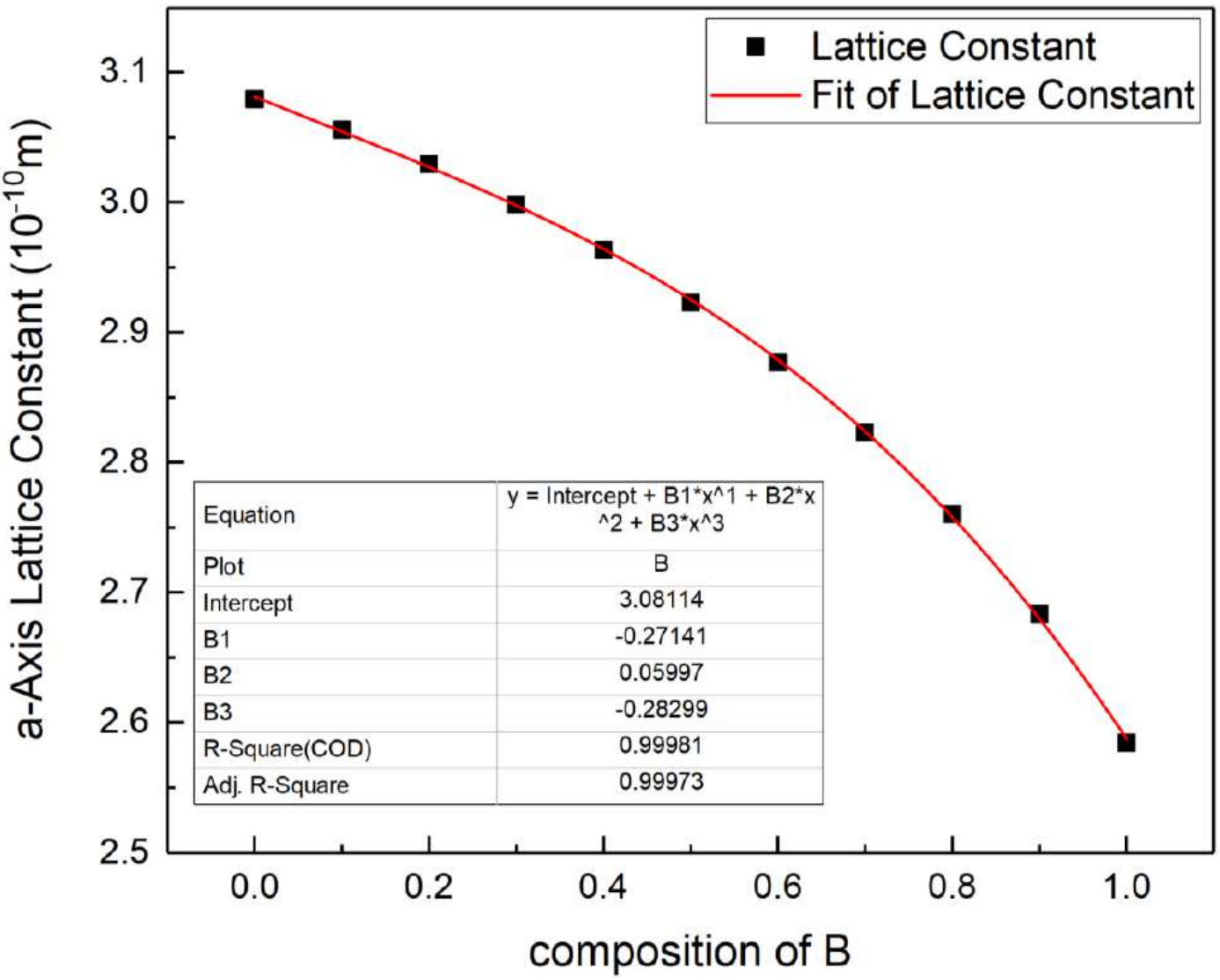

Figure 4

lattice constant of a-Axis changing with B composition