Computational Materials Science 130 (2017) 232–241

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Electronic and thermoelectric properties of the group-III nitrides (BN, AlN and GaN) atomic sheets under biaxial strains

Zheng Huang [a], Tie-Yu Lü [a,*], Hui-Qiong Wang [a,b], Shuo-Wang Yang [c], Jin-Cheng Zheng [a,b,d,*]

[a] Department of Physics, and Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen University, Xiamen 361005, China
[b] Xiamen University Malaysia, 439000 Sepang, Selangor, Malaysia
[c] Institute of High Performance Computing, Agency for Science, Technology and Research, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Republic of Singapore
[d] Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:
Received 17 July 2016
Received in revised form 22 December 2016
Accepted 9 January 2017

Keywords:
Thermoelectric properties
2D structure
Strain engineering
BN
AlN
GaN

ABSTRACT

Based on first-principles methods and Boltzmann transport theory, we investigated the biaxial strain effects on electronic and thermoelectric properties of three group-III nitrides (BN, AlN and GaN) 2D honeycomb mono-layered nanosheets. The direct-indirect band gap transitions occurred for BN and GaN nanosheets when the strain was applied. In addition, the band gaps decreased with increase of tensile strain; and we uncovered the mechanism behind by the total and projected density-of-state (PDOS) analyses. At the same time, we presented the contour plots of their electrical transport properties as a function of both temperature and carrier concentration at strain-free states. Power-factors of BN, AlN and GaN nanosheets were also calculated. We found only peak power factors of p-type GaN and n-type BN showed a strong dependence on biaxial strain. Such differences of the strain-dependent thermoelectric performance among BN, AlN and GaN may be due to the competition between covalency and ionicity in these 2D structures. Our results provide a new avenue to optimize thermoelectric properties of 2D nanosheets by strain engineering.

1. Introduction

Thermoelectric (TE) materials have been attracting a lot of attentions in recent years because of their ability to convert heat energy into electricity with reduced pollution [1–5]. The efficiency of TE materials is defined as the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$. Here T, S, σ and κ represent absolute temperature, Seebeck coefficient, electrical conductivity and thermal conductivity, respectively [4]. The thermal conductivity κ consists of the lattice thermal conductivity κ_l, and the electronic conductivity κ_e. To achieve high thermoelectric performance, ZT, the power-factor (PF) σS^2 is the key factor.

A high ZT is required for an-efficient conversion from thermal to electrical energy. Hence, high S, high σ and low κ are required. However, there exist opposing interactions between electrical conductivity σ, Seebeck coefficient S, and thermal conductivity κ. Generally, increasing S will result in decreasing σ, while decreasing σ also decreases electronic part of κ. Therefore, promoting ZT value is a challenging task in science and technology. Various strategies have been proposed to enhance ZT values. For example, the phonon-glass behaviors are found in caged compounds [6], grain boundary [7] and band convergence effects [8]. The strong electron–phonon coupling by charge density waves [9], liquid-like state [10], and nanostructures designing [3,11] methods were also widely used.

In addition, TE power generation requires efficient, chemically and thermally stable materials at high temperatures for ambient applications. III-nitrides, especially GaN, fulfill these criteria and they are potential high temperature TE materials [12–16]. Their thin films [17] and thin film based nanostructures [18] have shown enhanced in-plane thermoelectric conductivity compared with the corresponding bulks. Meanwhile, BN honeycomb nanosheet has been approved to be a stable ionic monolayer [19]. As analogues, AlN and GaN monolayers are predicted to be stable, and their nano-films/sheets can undergo a transition from a wurtzite structure with sp^3 tetrahedral coordination to a graphitic structure with sp^2 trigonal planar coordination to remove the destabilizing dipole [20]. On the other hand, the strain is also an effective approach to modify the physical properties of materials, especially for semiconductors. In this work, based on DFT calculations and Boltzmann transport theory, we studied the effects of strain and chemical

* Corresponding authors at: Department of Physics, and Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen University, Xiamen 361005, China (T.Y. Lü and J.C. Zheng).
E-mail addresses: lty@xmu.edu.cn (T.-Y. Lü), jczheng@xmu.edu.cn (J.-C. Zheng).

http://dx.doi.org/10.1016/j.commatsci.2017.01.013
0927-0256/

modification on the electronic and the thermoelectric properties of XN (X = B, Al, Ga) honeycomb 2D nanosheets. Our work provides a new avenue in promotion of new 2D nanostructure designing and TE materials.

2. Computational method

The plane-wave method in the framework of density functional theory (DFT) as implemented in QUANTUM ESPRESSO code [21] is employed. GBRV pseudopotential library [22] are used for all atoms and the exchange-correlation approximation is evaluated through the Perdew-Burke-Ernzerh (PBE) functional [23]. A cutoff energy of 40Ry and a $12 \times 12 \times 1$ Monkhorst-Pack grid sampling of Brillouin zone (BZ) are used for the geometry optimization. A fine k-points sampling $30 \times 30 \times 1$ is used for the ground-state calculations. Fig. 1 shows the schematic diagrams for monolayer XN (X = B, Al, Ga). The interspacing between adjacent layers is 20 Å that is large enough to make the interaction between layers neglected. Biaxial strains, defined as $(a - a_0)/a_0$, are applied within the range of ±6% with respect to the equilibrium constant a_0.

Based on DFT calculations and Boltzmann transport theory (BTT) [24,25], the thermoelectric features of these nanosheets have been calculated. The BOLTZTRAP code is employed to perform these calculations. The thermoelectric properties are mainly related to the curvature of bands [26]. The actual value of band gap does not affect appreciably on the thermoelectric property, although the band gaps of semiconductors are underestimated in DFT calculations due to the ignoring of many-electron interactions. BTT has been successfully applied to evaluate the thermoelectric properties of PbTe [27,28], SnTe [27], GeTe [27] and ZnO nanofilms [29].

3. Results and discussion

The geometrical relaxation results for these nitride honeycomb 2D nanosheets with and without biaxial strain are shown in Fig. 2. The lattice constants of BN, AlN and GaN at strain-free state are 2.51 Å, 3.13 Å and 3.21 Å, respectively. Our PBE results are very close to those of LDA [30]. The nonplanarity in Fig. 2 is defined as the distance between two neighboring atoms along c-axis after relaxation. The initial distance of two neighboring atoms is set to 1 Å, which is around 5% of two original neighboring atoms distance. It is shown that the atoms will go back to zero out-of-plane displacement after relaxation, meaning that these 2D structures against c-axis strains are stable enough. The slight fluctuation of GaN under compression may be due to its relatively high ionicity.

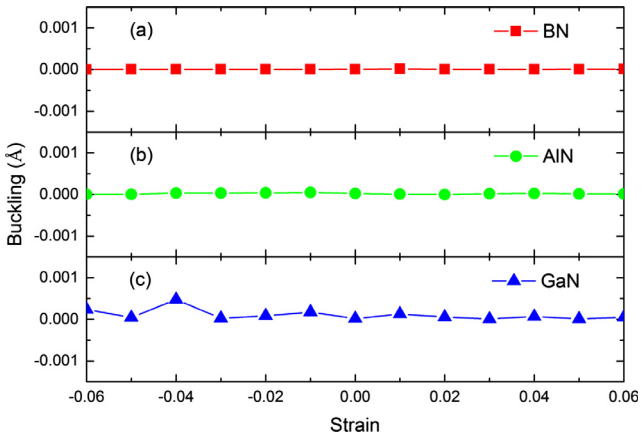

Fig. 2. Optimization results for BN, AlN and GaN 2D nanosheets. Horizontal coordinate is the in-plane strain, and the nonplanarity is the distance between two neighboring atoms along c-axis.

The band structures of BN, AlN and GaN nanosheets, with (±6%) and without strains, are given in Fig. 3. It can be seen that all of these three nanosheets have indirect band gaps at strain-free states, with the valence band maximum (VBM) at the K point, and the conduction band minimum (CBM) at the Γ point. This is in good agreement with the LDA results reported by Sahin [30]. While, at 6% strain (enlargement), the CBM of BN moves from Γ to K points; and the VBM of GaN moves from Γ to K points at −6% strain (compression). Interestingly, the AlN does not show such movements under strains within −6% to 6%.

For clear analysis, we plot the electron band edges at Γ-K-M k-points for aforementioned structures (see Fig. 4). It is seen that the area within the band gap of BN nanosheet forms an arc shape along strain increasing from −6% to 6%.This character is also reported in pervious works [31,32] but the peak of the arc locates at different strain states, which may attribute to the different potentials. Fig. 4a shows an indirect-direct band transition (from K-Γ to K-K), which is corresponding to the orbital variation of the VBM states due to the applied tensile strain. However, AlN nanosheet is found to keep indirect band gap and have a monotone but nonlinear decrease in band gaps with strain increases [Fig. 4b], which agrees well with previous reports [31,33]. Meanwhile, an indirect-direct band gap transition was found for GaN nanosheet at −4% strain. These results are consistent with previous work [33]. The decrease of the band gap can be attributed to the reduction of the orbits overlap because of the enlargement of Ga-N bond under strains. Actually, for all of these three nitride nanosheets, band gaps decrease with the increasing of the tensile strain.

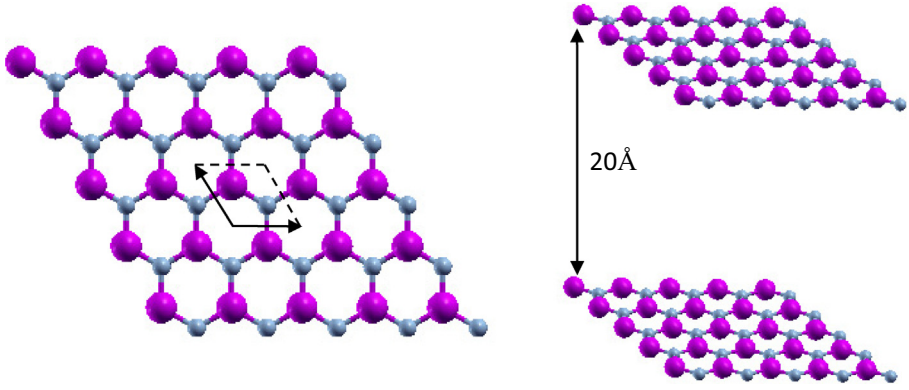

Fig. 1. The honeycomb monolayer model for nitrides. The two different colored balls state for two different types of atoms, c-axis is perpendicular to the monolayer plane, and the interlayer spacing between adjacent layers is 20 Å.