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The thermal and thermoelectric properties of in-plane C-BN hybrid structures and graphene/h-BN van der Waals heterostructures

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ABSTRACT

The two-dimensional nanomaterials graphene and hexagonal boron nitride (h-BN) have good thermal properties. When the two are combined together to form a planar C-BN hybrid structure or a van der Waals heterostructure due to the differences in crystal lattice and the electronic structure between graphene and h-BN, the new material is formed with novel thermal characteristics. We focus on the thermal properties of the two new materials as they change their configuration, size, and number of layers and review these novel characteristics.

In microelectronics, the thermophysical properties of nanomaterials have an important influence on the performance of microelectronic devices. The thermal conductivity (TC), thermal resistance (TR), thermal rectification, and thermoelectric effects of nanomaterials affect the performance of microelectronic devices. Among the two-dimensional nanomaterials, graphene and hexagonal boron nitride (h-BN) have broad application prospects in micro-nanoscale device preparation due to their excellent mechanical, electrical, and thermal properties, especially when they are combined to form a planar heterojunction and vertical stacking of van der Waals heterostructures. Thermal properties such as TC (k), TR, thermal rectification, and thermoelectric effect (ZT) have been shown to be significantly different between graphene and h-BN materials in these composite systems.

On the other hand, thermoelectric devices are distinguished from traditional refrigeration and power generation devices by virtue of their low pollution, stable operation, and low maintenance cost. The quality factor is an important parameter to measure the performance of thermoelectric devices. It is expressed as: [1]

$$ZT = \frac{S^2\sigma}{k}T$$

$\boldsymbol{S}$ is the Seebeck coefficient, $\boldsymbol{\sigma}$ is the electrical conductivity of the thermoelectric material, $\boldsymbol{T}$ is the absolute temperature, and $\boldsymbol{k}$ is the TC. Therefore, to improve the thermoelectric conversion efficiency of a thermoelectric device, a large Seebeck coefficient S, a high electrical conductivity σ, and a low TC k are required. This requires the reduction of the TC of the material as much as possible without affecting the electrical conductivity, thereby improving the quality of the thermoelectric device. In addition, heat capacity, TC, and thermal interface resistance are all factors that affect the thermoelectric material [1,2]. Both graphene and two-dimensional h-BN have high thermal conductivities and other physicochemical properties required as thermoelectric materials.

This article focuses on the TC, TR, and thermoelectric properties and applications of in-plane graphene/h-BN hybrid heterojunction, and vertical graphene/h-BN van der Waals heterostructure reveals the nature of the thermal properties of two-dimensional

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nanomaterials in the micro-nanoscale. In addition, we review their thermal properties, TR, thermal rectification, thermoelectric properties, and related thermal properties and latest applications.

1. Two-dimensional nanomaterials: graphene and h-BN

1.1. Structure and thermal properties of graphene

The ideal graphene is a two-dimensional crystal with a honeycomb-like hexagonal configuration with a single atomic layer thickness. The 2s electrons of each carbon atom and the $2p_x$ and $2p_y$ electrons form σ bonds by *sp* [2] orbital hybridization. The $3p_z$ orbital electrons that did not participate in hybridization form large π bonds delocalized perpendicular to this plane [3–9]. A strong interaction between the carbon atoms when subjected to external forces maintains the original hexagonal structure, and this stable structure also gives graphene good TC. The graphene electronic structure under tight binding depends mainly on the electrons of the π orbital [10–12]. A atoms and B atoms are two kinds of carbon atoms that are not equivalent in graphene (Fig. 1a). The bond length was 1.420 Å, and the lattice constant was 2.460 Å [13–15]. Based on the tight binding approximation, the band structure of graphene was obtained (Fig. 1b). The band diagram directly reflects that graphene is a zero-band gap two-dimensional crystal.

Its unique electronic structure gives graphene peculiar thermal characteristics. Studies have shown that the TC of graphene is as high as 3500–5300 W/mK [16,17]. The average mean free path (MFP) of phonons at room temperature is 775 nm, which is the main contribution to the thermal conduction of graphene. The interfacial scattering effect of the substrate in graphene leads to a decrease in the TC of the olefins [18–21]. Theoretical studies have shown that the high TC of graphene comes from the ballistic transport of its phonons, and its TC decreases with the increase in the number of graphene layers [17,22–25]. The thermal properties of graphene are affected by the influence of the boundary configuration and size [26,27]. In the micro-nanoscale range, the negative differential TC, TR, thermal rectification effect, and thermoelectric characteristics of graphene undergo great changes [28–30].

1.2. Structure and thermal properties of h-BN

Two-dimensional h-BN belongs to the hexagonal system. *B* atoms and **N** atoms form an extremely strong covalent bond in the layer by *sp* [2] hybridization to form a regular honeycomb hexagonal structure [31,32]. The *B* atoms and *N* atoms in single-layer h-BN are alternately arranged. The *B-N* bond length is 0.144 nm, the lattice constant is 0.2504 nm, the interlayer spacing is 0.333 nm, and the layers are connected by weak van der Waals forces (Fig. 2a) [32–37]. The layers easily peel, are non-conductive, and have a wide band gap (5.1ev, Fig. 2b), Mohs hardness of 2, high melting point, and high temperature reaching 2000°C. Thermal performance along the **C** axis is better. As the number of layers increases,

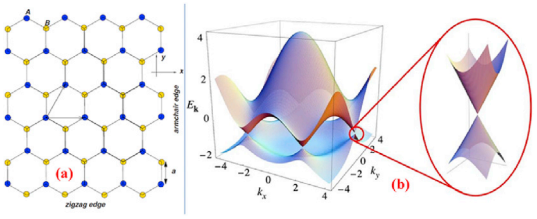

Fig. 1. (a) The graphene nanoribbons with zigzag edge and armchair edge [12]. (b) The band structure of graphene. The inset show the Dirac point, where is the intersection of the conduction band and the valence band [12].

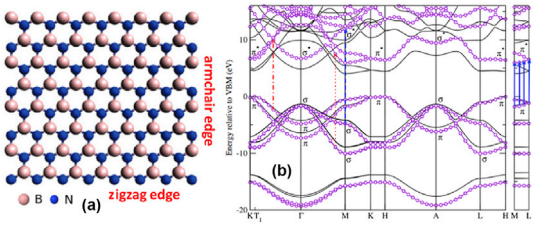

Fig. 2. (a) The structure of 2D h-BN with zigzag edge and armchair edge [32]. (b) The electronic band structure along high-symmetry lines for bulk h-BN [36]. h-BN, hexagonal boron nitride; VBM, valence band maximum.

the TC decreases because of the scattering of phonons due to the layered structure.

In two-dimensional nanomaterials, the TC of h-BN is second only to that of graphene. Studies have shown that a single layer of h-BN' s TC is up to 600 W/mK at room temperature [38]. When the number of layers increases to more than five, the TC of two-dimensional h-BN is 250 W/mK [39–42]. This value is close to the bulk TC of h-BN [43]. In addition, in the nanoscale range, the thermal properties of h-BN are greatly affected by the size effect and the boundary effect. The thermal rectification effect of the triangular vacancy defects in the h-BN nanoribbons (BNNRs) also affects the TC of h-BN [44]. The TC of the zigzag BNNRs is 20% higher than that of the armchair BNNRs [45]. In the thermoelectric effect, BNNRs are used for ballistic thermal power transmission. The transport properties are significantly higher than those of graphene nanoribbons (GNRs), and the lattice defects and boundary chirality affect the thermoelectric properties of h-BN [46–50].

2. In-plane C-BN hybrid structure

The electronic properties of **C** atoms, **N** atoms, and **B** atoms determine the physical and chemical properties of both graphene and 2D h-BN. There is a strong ionic interaction between the **B** atoms and the **N** atoms, and the C atoms are covalently linked. Although the two have the same lattice structure, their crystal lattices are different. Whether they are composed of a single-layer C-BN hybrid structure or a double-layered graphene/h-BN heterostructure, the different structure and combination of the two have special significance for controlling the electrical, magnetic, and thermal properties of composite materials. This is a very important application value for the preparation of micro-nanoscale functional devices.

2.1. The structure of monolayer C-BN hybrids

Although two-dimensional h-BN and graphene lattice are similar, graphene is a typical semiconductor without a band gap, and h-BN is an insulating material with a band gap of 5.97 eV [51]. The C-C bond length (0.142 nm) is slightly smaller than the B-N bond length (0.144 nm), resulting in a lattice mismatch of only 1.7%. Owing to the lattice mismatch between the two, they display different behavior from h-BN and graphene, both when they are complexed as a monolayer C-BN hybrid structure in physical characteristics [51–81].

2.1.1. In-plane monolayer C-BN hybrid structures

No matter how the system is combined, the appearance of such superlattices contains two types of interfaces, B/C or N/C. These two different interfaces play a key role in regulating the electronic properties of the system [51–81]. Theoretical work shows that when BNNRs are embedded in zigzag GNRs to form a monolayer