Carbon 113 (2017) 108–113

Contents lists available at ScienceDirect

Carbon

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

Thermoelectric properties of γ-graphyne from first-principles calculations

P.H. Jiang, H.J. Liu*, L. Cheng, D.D. Fan, J. Zhang, J. Wei, J.H. Liang, J. Shi

Key Laboratory of Artificial Micro- and Nano-Structures of Ministry of Education, School of Physics and Technology, Wuhan University, Wuhan 430072, China

ARTICLE INFO

Article history:
Received 18 August 2016
Received in revised form
16 November 2016
Accepted 17 November 2016
Available online 17 November 2016

ABSTRACT

The two-dimensional graphene-like carbon allotrope, graphyne, has been recently fabricated and exhibits many interesting electronic properties. In this work, we investigate the thermoelectric properties of γ-graphyne by performing first-principles calculations combined with Boltzmann transport theory for both electron and phonon. The carrier relaxation time is accurately evaluated from the ultra-dense electron-phonon coupling matrix elements calculated by adopting the density functional perturbation theory and Wannier interpolation, rather than the generally used deformation potential theory which only considers the electron-acoustic phonon scattering. It is found that the thermoelectric performance of γ-graphyne exhibits a strong dependence on the temperature and carrier type. At an intermediate temperature of 600 K, a maximum *ZT* value of 0.77 can be achieved for the *n*-type system and can be further enhanced to 1.4 by considering isotopic effect.

1. Introduction

The steady increase in the world's population and its demands for fuel and products cause energy crisis in the past 50 years. Moreover, many industrial and commercial energy utilizations result in excessive rates of waste heat rejection. The thermoelectric technology is believed to be one of the effective methods for energy harvesting since it provides a promising route to convert waste heat into electricity. The efficiency of a thermoelectric material is determined by the dimensionless figure-of-merit $ZT = S^2\sigma T/(\kappa_e + \kappa_{ph})$, where S, σ, T, κ_e and κ_{ph} are the Seebeck coefficient, the electrical conductivity, the absolute temperature, the electronic and phonon thermal conductivity, respectively. Good thermoelectric material has larger *ZT* value and one therefore must try to maximize the power factor ($S^2\sigma$) and/or minimize the thermal conductivity ($\kappa_e + \kappa_{ph}$). However, it is extremely difficult to do so since these transport coefficients are usually coupled with each other in conventional thermoelectric materials [1]. In recent years, the successful fabrication of low-dimensional thermoelectric materials has simulated a lot of research interest [2–5] because the *ZT* value can be enhanced remarkably due to the quantum confinement effect [6,7]. On the other hand, it is highly desired that better thermoelectric performance could be realized in the earth-abundant and environment-friendly systems, e.g., carbon materials. In this respect, the two-dimensional graphene seems to be a possible choice since its first fabrication in 2004 [8]. The existence of Dirac-cone band structure makes graphene exhibit numerous novel electronic properties [9]. However, the absence of band gap leads to very smaller Seebeck coefficient of graphene. Together with extraordinarily high thermal conductivity, the thermoelectric performance of graphene is indeed extremely poor [10].

Another two-dimensional candidate in the carbon family is graphyne, which was first proposed theoretically by Baughman et al. in 1987 [11]. It can be viewed as modified graphene by inserting the carbon-carbon triple bonds (*sp* hybridization) into the sp^2 hybridized graphene. A series of atomic structures, e.g., the α-, β-, γ-, 6, 6, 12-graphyne and graphdiyne, can be obtained by varying the number and position of the triple bonds [11,12]. Recently, the successful fabrication of large area graphyne films [13] has inspired extensive studies exploring its mechanical, thermal, electronic and optical properties [14–17]. Compared with graphene, graphyne exhibits more amazing electronic properties since the Dirac cones with different symmetries are presented [15]. Moreover, the band gap is opened up in the γ-graphyne and graphdiyne [18,19]. Such novel characteristics extend the application prospects of the two-dimensional carbon allotropes. The presence of a band gap can

---

* Corresponding author.
E-mail address: phlhj@whu.edu.cn (H.J. Liu).

http://dx.doi.org/10.1016/j.carbon.2016.11.038

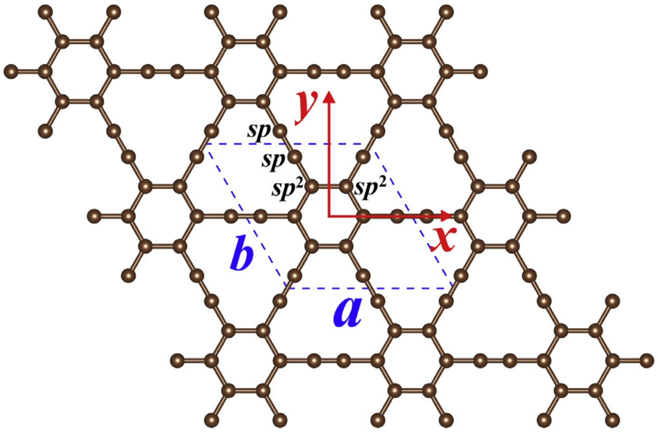

Fig. 1. The atomic structure of γ-graphyne. The blue dashed lines indicate the primitive cell with basis vectors ***a*** and ***b***. The conventional *x*- and *y*-axis are also indicated. (A colour version of this figure can be viewed online.)

drastically increase the Seebeck coefficient [20], and the inserted triple bonds can reduce the thermal conductivity significantly [19,21,22]. All these observations suggest that the graphyne systems with finite band gap could exhibit very favorable thermoelectric performance, as already demonstrated by a recent work of Tan et al. [19]. Although the carrier relaxation time in their work is somehow overestimated, they stimulated new interests and offered useful reference to explore the carbon-based thermoelectric materials both theoretically and experimentally.

In this work, the thermoelectric properties of the semiconducting γ-graphyne is systematically investigated by using first-principles calculations and Boltzmann transport theory, where the carrier relaxation time is accurately evaluated from the ultra-dense electron-phonon coupling matrix elements. We demonstrate that the thermoelectric performance of γ-graphyne exhibits a marked dependence on the temperature and carrier type. At an intermediate temperature of 600 K, a maximum *ZT* value of 1.4 can be achieved for the *n*-type system by isotopic substitution, which suggests that good thermoelectric performance can be also achieved in previously unexpected carbon systems.

2. Computational methods

Our first-principles total energy calculations are performed within the framework of density functional theory (DFT), as implemented in the QUANTUM ESPRESSO package [23]. We use the norm-conserving pseudopotential and the exchange-correlation functional is in the form of Perdew-Burke-Ernzerhof [24]. The system is modeled by adopting a hexagonal supercell geometry where the vacuum distance is set to 14 Å to eliminate the interactions between the graphyne layer and its periodic images. The kinetic energy cutoff is 80 Ry for the wavefunction and 800 Ry for the charge density. For the phonon dispersion relations and the electron-phonon coupling matrix elements, we apply the density functional perturbation theory (DFPT) [25] and Wannier interpolation technique [26]. The calculations are initially done by using a coarse 6 × 6 × 1 **q** and **k** mesh, and then interpolate to a dense mesh of 120 × 120 × 1 via the maximally localized Wannier functions as implemented in the electron-phonon Wannier (EPW) package [27]. After obtaining the electron self-energy $\Sigma_{n\mathbf{k}}$ for band *n* and state **k** from the interpolated ultra-dense electron-phonon coupling matrix elements, the relaxation time can be readily determined by $(\tau_{n\mathbf{k}})^{-1} = 2[\mathrm{Im}(\Sigma_{n\mathbf{k}})]/\hbar$ [28], where $\hbar$ is the reduced Plank constant.

Based on the energy band structure and carrier relaxation time, the electronic transport coefficients can be calculated by using the following formulas as derived from Boltzmann theory [29] under the rigid-band picture:

$$S = -\frac{1}{eT}\frac{\sum_{n,\mathbf{k}}\left(E_{n\mathbf{k}} - E_f\right)v_{n\mathbf{k}}^2\tau_{n\mathbf{k}}\frac{\partial f_{n\mathbf{k}}}{\partial E_{n\mathbf{k}}}}{\sum_{n,\mathbf{k}} v_{n\mathbf{k}}^2\tau_{n\mathbf{k}}\frac{\partial f_{n\mathbf{k}}}{\partial E_{n\mathbf{k}}}}, \tag{1}$$

$$\sigma = \frac{1}{NV}\sum_{n,\mathbf{k}} -e^2 v_{n\mathbf{k}}^2\tau_{n\mathbf{k}}\frac{\partial f_{n\mathbf{k}}}{\partial E_{n\mathbf{k}}}, \tag{2}$$

Here $E_{n\mathbf{k}}$ is the energy eigenvalue, E_f is the fermi energy, $v_{n\mathbf{k}}$ is the group velocity, $\tau_{n\mathbf{k}}$ is the relaxation time, $f_{n\mathbf{k}}$ is the Fermi occupation, *N* is the total number of **k** points, and *V* is the volume of the primitive cell. The electronic thermal conductivity κ_e is derived from the electrical conductivity σ according to the Wiedemann-Franz Law $\kappa_e = L\sigma T$ [30], where the Lorenz number *L* for the two-dimensional system is expressed as [6]:

$$L = \frac{\kappa_e}{\sigma T} = \left(\frac{k_B}{e}\right)^2\left[\frac{3F_2}{F_0} - \left(\frac{2F_1}{F_0}\right)^2\right]. \tag{3}$$

with the Fermi integral $F_i = F_i(\eta) = \int_0^\infty \frac{x^i \mathrm{d}x}{e^{(x-\eta)}+1}$ (η is the reduced Fermi energy).

The phonon thermal conductivity κ_{ph} can be obtained by solving

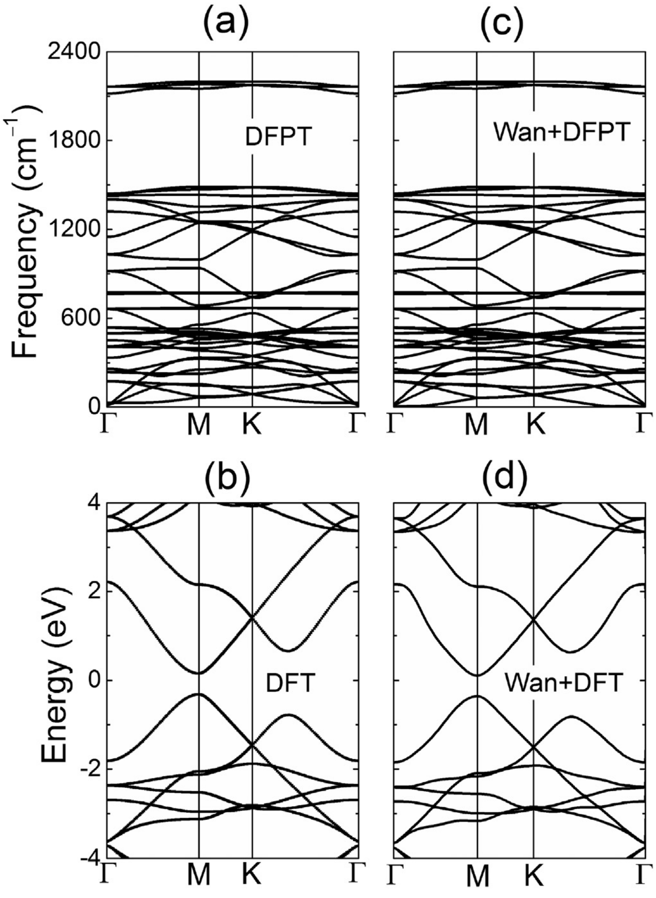

Fig. 2. The phonon dispersion relations and electronic band structures of γ-graphyne calculated by using (a) DFPT, (b) DFT, (c) Wannier interpolations based on DFPT (Wan + DFPT), and (d) Wannier interpolations based on DFT (Wan + DFT).