Biaxial tensile strain tuned up-and-down behavior on lattice thermal conductivity in $\beta$-AsP monolayer

San-Dong Guo© and Jun Dong

School of Electronic Engineering, Xi’an University of Posts and Telecommunications, Xi’an 710121, People’s Republic of China

E-mail: guosd@cumt.edu.cn

Received 28 March 2018, revised 5 May 2018
Accepted for publication 16 May 2018
Published 12 June 2018

Abstract
Various two-dimensional (2D) materials with a graphene-like buckled structure have emerged, and the $\beta$-phase AsP monolayer has been recently proposed to be thermodynamically stable from first-principles calculations. The studies of thermal transport are very useful for these 2D materials-based nano-electronics devices. Motivated by this, a comparative study of strain-dependent phonon transport of AsP monolayers is performed by solving the linearized phonon Boltzmann equation within the single-mode relaxation time approximation (RTA). It is found that the lattice thermal conductivity ($\kappa_L$) of the AsP monolayer is very close to the one of As monolayer with a similar buckled structure, which is due to neutralization between the reduction of phonon lifetimes and group velocity enhancement from As to AsP monolayer. The corresponding room-temperature sheet thermal conductance of AsP monolayer is 152.5 W K$^{-1}$. It is noted that the increasing tensile strain can harden a long wavelength out-of-plane (ZA) acoustic mode, and soften the in-plane longitudinal acoustic (LA) and transversal acoustic (TA) modes. Calculated results show that $\kappa_L$ of AsP monolayer presents a nonmonotonic up-and-down behavior with increased strain. The unusual strain dependence is due to the competition among the reduction of phonon group velocities, improved phonon lifetimes of ZA mode and nonmonotonic up-and-down phonon lifetimes of TA/LA mode.

1. Introduction
Due to the great importance for new-generation high performance electronic devices, transition-metal dichalcogenide (TMD) [1], group IV–VI [2], group-VA [3, 4] and group-IV [5] monolayers have been widely investigated both theoretically and experimentally. Compared with graphene as a representative 2D material, group-VA monolayers are semiconductors with significant intrinsic band gaps, which have potential applications for electronic, optoelectronic, thermoelectric and energy devices [6]. Phosphorene (P monolayer) is a classic group-VA monolayer with a direct band gap of 2.0 eV and a high hole mobility above $10^4$ cm$^2$ V$^{-1}$ s$^{-1}$ [7–10]. Shortly after phosphorene, group-VA arsenene (As
monolayer), antimonene (Sb monolayer) and bismuthene (Bi monolayer) with desirable stabilities and high carrier mobilities are predicted by first-principle calculations [3]. Subsequently, the antimonene of them is fabricated experimentally on various substrates via van der Waals epitaxy growth [4, 11, 12]. Recently, AsSb, SbBi and AsP monolayers have also been identified as novel 2D semiconductors in theory [13–16]. Under biaxial strain, a quantum spin Hall insulator can be achieved in monolayer β-BiSb and β-SbAs [13, 15]. It is also predicted that giant tunable Rashba spin splitting can be realized in the BiSb monolayer [14]. The AsP monolayer with direct band gap and very high mobility is predicted as a promising 2D solar cell donor [16].

As is well known, thermal transport is a key factor for the performance of nano-devices. To effectively remove the accumulated heat, a high thermal conductivity is needed. However, a material with low thermal conductivity has potential applications in the thermoelectric field. In theory, thermal transports of group-VA monolayers have been widely studied for both electron and phonon parts [17–25]. The α-arsenene and antimonene show anisotropic $\kappa_L$ along the zigzag and armchair directions [18, 20]. It has been proved that chemical functionalization is an effective way to reduce $\kappa_L$ of antimonene [22]. The thermoelectric properties of group-VA monolayers have also been performed by first principle calculations [21, 23, 25], and suggest they are potential candidates for thermoelectric application. Compared with many 2D materials, bismuthene has very low $\kappa_L$, which is very important for thermoelectric applications [21]. It is also predicted that the SbAs monolayer has a lower $\kappa_L$ than arsenene or antimonene [24]. In nanoscale devices, the residual strain usually exists in real applications [26], which can produce important effects on the intrinsic physical properties of 2D materials. The strain dependent transport properties have been investigated in lots of 2D materials [19, 27–34]. The power factor can be improved by strain in MoS$_2$, PtSe$_2$ and ZrS$_2$ monolayers due to bands converging [27–29]. Tensile strain can induce strong size effects on $\kappa_L$ of antimonene, silicene, germanene and stanene [19, 32]. With increased strain, the $\kappa_L$ shows a monotone decrease (pentagraphene), and the strength of interaction among the three phonon velocities, enhanced phonon lifetimes of the ZA branch and nonmonotonic up-and-down phonon lifetimes of the TA/LA branch.

The first-principles calculations are performed within the projector augmented-wave method, as implemented in the VASP code [35, 36, 38]. The generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE-GGA) is adopted as exchange-correlation functional [37]. A $20 \times 20 \times 1$ k-mesh is used during structural relaxation, with a Hellman–Feynman × 1 eV cutoff. The generalized gradient approximation is carried out by using Phonopy + VASP codes [35, 36, 38, 39]. By solving the linearized phonon Boltzmann equation, the $\kappa_L$ is computed with single-mode RTA by the Phonopy code [39]. The $\kappa_L$ can be expressed as:

$$\kappa = \frac{1}{NV_0} \sum_\lambda \kappa_\lambda = \frac{1}{NV_0} \sum_\lambda C_\lambda \nu_\lambda \times \nu_\lambda \tau_\lambda$$ (1)

in which $\lambda$, $N$ and $V_0$ are thephonon mode, the total number of $q$ points sampling Brillouin zone (BZ) and the volume of a unit cell, respectively, and $C_\lambda$, $\nu_\lambda$, $\tau_\lambda$ are the specific heat, phonon velocity and phonon lifetime. $C_\lambda$ is the mode dependent heat capacity, which can be attained by:

$$C_\lambda = k_B \left( \frac{h \omega_\lambda}{k_B T} \right)^2 \exp\left( \frac{h \omega_\lambda}{k_B T} \right) \left[ \exp\left( \frac{h \omega_\lambda}{k_B T} \right) - 1 \right]^2$$ (2)

where $k_B$ and $h$ are the Boltzmann constant and reduced Planck constant. $\nu_\lambda$ can be obtained directly from the eigenvalue equation:

$$\frac{\partial \omega_\lambda}{\partial q} \equiv \nu_\lambda.$$ (3)

The phonon lifetime $\tau_\lambda$ can be attained by the phonon linewidth $2\Gamma_\lambda(\omega_\lambda)$ of the phonon mode $\lambda$:

$$\tau_\lambda = \frac{1}{2\Gamma_\lambda(\omega_\lambda)}.$$ (4)

$\Gamma_\lambda(\omega)$ takes the form analogous to the Fermi golden rule:

$$\Gamma_\lambda(\omega) = \frac{18\pi}{h^2} \sum_{\lambda' \lambda''} |\Phi_{-\lambda\lambda'\lambda''}|^2 [(f_\lambda^* + f_{\lambda''} + 1) \delta(\omega - \omega_\lambda^*) - f_\lambda \delta(\omega - \omega_\lambda^*) - \delta(\omega - \omega_\lambda^* + \omega_\lambda^*)]$$ (5)

in which $f_\lambda$ and $\Phi_{-\lambda\lambda'\lambda''}$ are the phonon equilibrium occupancy and the strength of interaction among the three phonons $\lambda$, $\lambda'$, and $\lambda''$ involved in the scattering. Based on the supercell approach with finite atomic displacement of 0.03 Å,
the second-order interatomic force constants (IFCs) can be attained by using a $5 \times 5 \times 1$ supercell with k-point meshes of $2 \times 2 \times 1$. According to second-order harmonic IFCs, phonon dispersions can be calculated by the phonopy package [40], determining the allowed three-phonon scattering processes. The third-order IFCs can be attained by using a $4 \times 4 \times 1$ supercell with k-point meshes of $3 \times 3 \times 1$, which is related to the three-phonon scattering rate. To accurately compute the lattice thermal conductivity, the reciprocal spaces of the primitive cells are sampled by $100 \times 100 \times 1$ meshes. For 2D materials, the calculated $h$ depends on the length of the unit cell along the z direction [41]. They should be normalized by multiplying $Lz/d$, where $Lz$ is the length of unit cell along the z direction, and $d$ is the thickness of 2D material. However, the $d$ is not well defined, for example, graphene. In this work, the $Lz = 18$ Å is used as $d$. By $\kappa \times d$, the thermal sheet conductance can be attained.

3. Main calculated results and analysis

Like monolayers, the $\beta$-AsP monolayer (No. 156) has a graphene-like buckled honeycomb structure, which has a lower symmetry compared with the As monolayer (No. 164). The AsP monolayer can be built by replacing one sublayer of As monolayer with P atoms. The schematic crystal structure of AsP monolayer is plotted in figure 1, and the unit cell is constructed with the vacuum region of more than 15 Å to avoid spurious interaction between neighboring layers. The optimized lattice constant (buckling parameter) is $a = b = 3.45$ Å ($h = 1.33$ Å), which is about 4.4% (5.0%) lower than that of the As monolayer.

The elastic properties of 2D materials have been widely studied [3, 14, 16, 42–45]. For As and AsP monolayers, two independent elastic constants $C_{11} = C_{22}$ and $C_{12}$ are calculated using the stress-strain relations. The 2D Young’s moduli $Y^{2D}$ and shear modulus $G^{2D}$ are given [42]:

$$Y^{2D} = \frac{C_{11} - C_{12}}{C_{11}}$$

(6)

$$G^{2D} = C_{66}$$

(7)

$$C_{66} = (C_{11} - C_{12})/2.$$  

(8)

The corresponding Poisson ratios can be expressed as:

$$\nu^{2D} = \frac{C_{12}}{C_{11}}.$$  

(9)

The related data of As and AsP monolayers are listed in table 1, which agree well with available theoretical values [3, 16]. It is found that $C_{11}$, $G^{2D}$ and $Y^{2D}$ of the AsP monolayer are very close to the ones of As monolayer, while $C_{12}$ and $\nu$ are lower for AsP than the As monolayer. The $G^{2D}$ and $Y^{2D}$ of the AsP monolayer are significantly lower than ones of h-BN and graphene [42, 45] due to weaker As-P bonds compared to B-N and C-C bonds, but they are close to ones of silicene. However, those of the AsP monolayer are larger than ones of the BiSb monolayer with a similar crystal structure [14]. Finally, the related data of graphene and silicene [42] also are listed in table 1.

The phonon dispersion curves of As and AsP monolayers along the high symmetry path (Γ-K-M-Γ) are shown in figure 2, which agree well with previous theoretical results [3, 16]. The three acoustic and three optical phonon branches can...
be observed due to two atoms in the unit cell. It is a general feature of 2D material that LA and TA branches are linear near the $\Gamma$ point, while the ZA branch deviates from linearity [19, 27–34]. Based on the elastic theory, the ZA phonon branch should have quadratic dispersion when the sheet is free of stress [46, 47]. However, the As and AsP monolayers have linear components in the dispersions of ZA branches. There are two possible reasons for additional linear components. In Phonopy and Phono3py codes, the IFCs are only corrected by small stress [46, 47]. However, the As and AsP monolayers have the same thickness (18 $\AA$). Their thermal sheet conductances [41] are 152.5 W K$^{-1}$ and 154.6 W K$^{-1}$, which are lower than the one of graphene (12450.61 W K$^{-1}$), but are higher than the one of silicene (118.86 W K$^{-1}$) [45]. Our calculated $\kappa_L$ of the As monolayer is in the range of the previous ones [18, 45]. It is expected that the $\kappa_L$ of the AsP monolayer is higher than one SbAs monolayer (28.8 W K$^{-1}$) [24]. The relative contributions of every phonon mode to the total $\kappa_L$ for As and AsP monolayers (300 K) are plotted in figure 3. It is clearly seen that the acoustic branches of both As and AsP monolayers dominate $\kappa_L$, about 97.5% and 96.7%. For the As monolayer, the contribution among three acoustic branches has little difference, about 32.3%, 34.4% and 30.9% from ZA to TA to LA branch. For AsP monolayer, the TA branch (40.2%) has a larger contribution than ZA (27.9%) and LA (28.6%) branches. This is obviously different from the SbAs monolayer with very little contribution to the total $\kappa_L$ from ZA branch, only 2.4% [24].

To understand the almost the same $\kappa_L$ between the As and AsP monolayers, the phonon mode group velocities and lifetimes are calculated. Due to the dominant contribution from the acoustic branches, only the acoustic phonon mode group velocities and lifetimes are shown in figure 4. It is clearly seen that most of the group velocities for the AsP monolayer are larger than those of the As monolayer, due to stiffened acoustic phonon modes, which result in the increase of $\kappa_L$. From the As to AsP monolayer, the largest phonon group velocity of LA/TA modes increases from 3.04/4.63 km s$^{-1}$ to 3.91/5.84 km s$^{-1}$ near the $\Gamma$ point, and the largest phonon group velocity of ZA branch changes from 2.18 km s$^{-1}$ to 2.71 km s$^{-1}$. However, most of the phonon lifetimes of the AsP monolayer are shorter than those of the As monolayer, which results in the decrease of $\kappa_L$. The shorter phonon lifetimes for AsP than for the As monolayer can be understood by phonon anharmonicity. The anharmonic nature of structures can be roughly quantified by the Grüneisen parameter ($\gamma$), and phonon mode Grüneisen parameters of As and AsP monolayers are plotted in figure 5. The magnitude of $\gamma$ for the AsP monolayer is obviously larger than the As monolayer, which means a stronger phonon anharmonicity in the AsP monolayer, giving rise to the shorter phonon lifetime of AsP monolayer. In a word, the reduction of phonon lifetimes from As to AsP monolayers neutralizes the positive effect of the group velocity enhancement, producing almost the same $\kappa_L$ between the As and AsP monolayer. Since P and As are in the same group, the difference between their atomic interaction potential can be ignored. As is heavier than P in terms of atomic mass, and thus it lowers the vibration frequency (mass: AsP < AsAs), leading to lower group velocities for As than AsP monolayers. The shorter phonon lifetimes for...
AsP than for the As monolayer are due to introducing phonon point defect scattering by considering monolayer AsP as an alloy, namely alloying As with P. It is noteworthy that almost exactly the same lattice thermal conductivity depends on the lattice constants of the As and AsP monolayer.

Strain dependence of $\kappa_L$ has been investigated in many 2D materials [19, 27–34]. Here, $\varepsilon = (a - a_0)/a_0$ is defined to describe biaxial strain effects on $\kappa_L$ of AsP monolayer, where $a_0$ is the unstrain lattice constant. The calculations are carried out on six values of $\varepsilon$ with tensile strain from 0% to 10%. Firstly, the stress is calculated as a function of strain, which is shown in figure 6. In the considered strain range, the stress is relatively small, about 3.1 nm$^{-1}$ for 10% strain, which can be easily realized experimentally. The relatively small stress caused by tensile strain is also found in the SbAs monolayer [24]. The elastic constants $C_{ij}$, Young’s moduli $Y$ and shear modulus $G$ versus strain for the AsP monolayer with strain from 0% to 10% are plotted in figure 6. It is found that $C_{11}$, $Y$ and $G$ firstly increase with strain from 0% to 2%, and then decrease. However, the $C_{12}$ monotonically decreases from 0% to 10% strain. In the considered strain range, they all satisfy the Born criteria of mechanical stability [42]:

$$C_{11} > 0, \ C_{66} > 0.$$  \hspace{1cm} (10)

The phonon dispersions along the high symmetry directions with strain from 0% to 10% are plotted figure 7. The calculated results show that no imaginary frequencies are observed with strain from 0% to 10%, which indicates that the strained AsP monolayer is dynamically stable. It is clearly seen that the dispersions of both TA and LA branches are softened with increasing strain, resulting in the reduction of phonon group velocity. However, the dispersion of ZA branch near $\Gamma$ point is stiffened with strain increasing, indicating the enhancement of phonon group velocity. A similar change of acoustic group velocities can be found in penta-graphene [31] and MoTe$_2$ [34]. It is noted that the quadratic nature of the ZA mode near the $\Gamma$ point turns into a straight line. A similar phenomenon can be observed in MoTe$_2$ [34]. The dispersions of optical branches overall move toward low energy with increasing the strain from 0% to 10%. The tensile strain can soften the optical, LA and TA modes, which is mainly due to the reduction of the material stiffness under tensile strain. Based on the elastic theory, in the presence of tension, the long-wavelength dispersion of ZA mode changes from $(\frac{k^2}{\rho})^{1/2}$ to $k\sqrt{\frac{\kappa}{\rho} k^2 + \frac{2}{\rho}}$, where $\kappa$, $\rho$ and $\gamma$ are the bending stiffness, 2D mass density and interfacial stiffness, respectively [50]. With increasing the tensile strain, the dispersion of the ZA mode becomes linear with $k$ trending towards 0 [50]. The $\gamma$ gap decreases from 4.46 THz to 2.58 THz with strain from 0% to 10%, which has important effects on acoustic + a coustic $\rightarrow$ optical (aao) scattering.

The $\kappa_L$ of the AsP monolayer in the strain range of 0%–10% as a function of temperature is shown in figure 8, along with the $\kappa_L$ versus strain at the temperatures of 200, 250, 300 and 400 K. In the considered strain range, $\kappa_L$ firstly increases with strain increasing, and then decreases. The critical strain is about 5%. Similar up-and-down behavior is also found in penta-SiC$_2$ [31] and bilayer graphene [51], and their peak value occurs at 5% and 3% tensile strain. The contribution of each mode to total $\kappa_L$ is calculated at different strains, and the acoustic branches dominate the $\kappa_L$ for all considered strains, about 96%. Therefore, we only show contributions from ZA, TA and LA acoustic branches versus strain in figure 9. The contribution from the ZA mode increases significantly with strain increasing, from 27.9% to 60.1%, while the contribution from the TA/LA mode decreases. For small (large) strains (<6%), the TA (ZA) mode has the largest contribution.

**Figure 5.** The phonon mode group Gruneisen parameter ($\gamma$) of As (black) and AsP (red) monolayers in the first BZ for ZA (square symbol), TA (circle symbol) and LA (upright triangle symbol) acoustic branches.

**Figure 6.** The stress (top) and elastic constants $C_{11}$, Young’s moduli $Y$ and shear modulus $G$ (bottom) versus strain for the AsP monolayer with strain from 0% to 10%.
When strain reaches 10%, the ZA mode contributes more than the LA and TA modes to the total \( \kappa_L \).

To identify the underlying mechanism of strain-dependent phonon transport of the AsP monolayer, phonon mode group velocities with 0%, 6% and 10% strains are plotted in figure 10. In the low frequency region, group velocities of the ZA mode increase with increasing strain, due to stiffened ZA dispersion. The group velocity of the ZA mode near \( \Gamma \) point increases from 0.69 km s\(^{-1}\) to 1.70 km s\(^{-1}\) to 2.02 km s\(^{-1}\) with strain from 0% to 6% to 10%. However, most of the group velocities of the ZA mode decrease in the high frequency region. For TA and LA branches, the reduction of phonon group velocities is observed due to softened phonon dispersions with increasing strain. The largest group velocity of TA (LA) mode reduces from 3.91 (5.84) km s\(^{-1}\) to 3.53 (5.07) km s\(^{-1}\) to 3.19 (4.49) km s\(^{-1}\), when strain changes from 0% to 6% to 10%. The reduction of most phonon group velocities would result in the decrease of \( \kappa_L \) with increased strain.

Next, the strain-dependent phonon lifetimes of the AsP monolayer are calculated by the three-phonon scattering rate from third-order anharmonic IFCs. The phonon lifetimes with 0%, 6% and 10% strains are plotted in figure 11. It is clearly seen that phonon lifetimes of the ZA mode present a monotonic increase upon increased strain, which supports the enhancement of ZA contribution. However, the phonon lifetimes firstly increase for TA and LA branches, and then drop down. With increasing strain, the buckling height decreases, which has two competing influences on phonon transport. On one hand, the decreased buckling height decreases ZA phonon scattering channels, producing increased phonon lifetimes. On the other hand, the acoustic-optical gap decreases with the decreased buckling height, which can strengthen acoustic \( \rightarrow \) acoustic \( \rightarrow \) optical scattering, leading to reduced phonon lifetimes. By combining strain dependence of phonon group velocities and...
phonon lifetimes, we can conclude that at low strains (<6%) the phonon lifetimes enhancement is the major mechanism responsible for increased $\kappa_L$, while at high strains (>6%) the reduction of group velocities as well as the decrease of the phonon lifetimes of LA and TA modes result in decreased $\kappa_L$. At low strains (<6%), the contribution from TA/LA has little change with increasing strain, which is because the enhanced phonon lifetimes partially neutralize the negative effect of the group velocity reduction. At high strains (>6%), the contribution of TA/LA rapidly decreases, which is due to the reduction of both group velocities and phonon lifetimes.

To study the size effect on $\kappa_L$, the cumulative $\kappa_L$ divided by total $\kappa_L$ with respect to phonon mean free path (MFP) are plotted in figure 12 with strain from 0% to 10% at 300 K. It is well known that the cumulative $\kappa_L$ divided by total $\kappa_L$ increases, and then approaches one. It is clearly seen that the saturated MFP increases from 95 nm to 490 nm with strain from 0% to 10%, which means that the phonons with longer MFP contribute to $\kappa_L$ with increased strain. This demonstrates that strain can effectively tune the size effects on $\kappa_L$ of the AsP monolayer. The strain-tuned strong size effects on $\kappa_L$ can also be found in antimonene, silicene, germanene and stanene [19, 32].

4. Conclusion

In summary, the first-principles calculations are performed to predict the strain-dependent $\kappa_L$ of the AsP monolayer. An almost the same $\kappa_L$ between As and AsP monolayer is observed, which is because the reduction of phonon lifetimes from the As to AsP monolayer cancels out the group velocity enhancement. It is found that the increased tensile strain can harden the long wavelength ZA acoustic branch, which may provide guidance on the fabrication of AsP monolayer by tensile strain. In fact, the Bi monolayer with the similar graphene-like buckled structure has been successfully synthesized by tensive strain [52]. Calculated results show that $\kappa_L$ of AsP monolayer firstly increases with strain increasing, and then decreases. The competition among group velocity reduction, phonon lifetime enhancement of the ZA mode and non-monotonic phonon lifetime of the TA/LA modes leads to the up-and-down behavior of $\kappa_L$. Our work enriches the studies of thermal transport of 2D materials with graphene-like buckled structures, and offers perspectives of tuning the thermal transport properties of AsP monolayers for applications such as in thermoelectrics and nanoelectronics.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grant No. 11404391) and Shaanxi Provincial Education Department (Program No. 17JF026). We are grateful to the Advanced Analysis and Computation Center of CUMT for the award of CPU hours to accomplish this work.

ORCID iDs

San-Dong Guo  https://orcid.org/0000-0002-4894-1585

References

[1] Chhowalla M, Shin H S, Eda G, Li J I, Loh K P and Zhang H 2013 Nat. Chem. 5 263
[2] Fei R X, Li W B, Li J and Yang L 2015 Appl. Phys. Lett. 107 173104
[3] Zhang M S L, Li F Y, Yan Z, Li Y F, Kan E J, Liu W, Chen Z F and Zeng H B 2016 Angew. Chem. 128 1698
[4] Ji J P et al 2016 Nat. Commun. 7 13352
[5] Balendhran S, Wali A, Nili H, Sriham S and Bhaskaran M 2015 Small 11 640
[6] Zhang S L et al 2018 Chem. Soc. Rev. 47 982–1021
[7] Fei R and Yang L 2014 Nano Lett. 14 2884
[8] Qiao J, Kong X, Hu Z X, Yang F and Ji W 2014 Nat. Commun. 5 4475
