Highly anisotropic thermoelectric properties of carbon sulfide monolayers

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Received 19 October 2018, revised 19 December 2018
Accepted for publication 7 January 2019
Published 29 January 2019

Abstract

Strain engineering applied to carbon monosulphide monolayers allows to control the bandgap, controlling electronic and thermoelectric responses. Herein, we study the semiconductor–metal phase transition of this layered material driven by strain control on the basis of first-principles calculations. We consider uniaxial and biaxial tensile strain and we find a highly anisotropic electronic and thermoelectric responses depending on the direction of the applied strain. Our results indicate that strain-induced response could be an effective method to control the electronic response and the thermoelectric performance.

Keywords: Seebeck coefficient, strain, electronic structure, bandgap engineering, 2d materials

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years new phenomena emerging from two-dimensional materials have been explored. Despite the exciting new electronic properties that make it possible to design new applications [1, 2], one of the biggest challenges ahead is to control bandgap in a systematic way. Several solutions are currently being considered such as doping [3, 4], stacking orders [5–8] or strain [9, 10]. Research into two-dimensional (2D) materials goes beyond graphene [11, 12]. On one hand, elements of the same carbon group have been considered to produce layered materials, for instance the silicene, germanene or stanene monolayers [13, 14]. On the other hand, the quest for new electronic properties in layered materials has been extended to the various phosphorus-based assemblies, in particular the black phosphorus monolayers or phosphorene may impact on future technologies [15]. Following these trends, our goal is to demonstrate the interesting properties of the recently predicted carbon sulfide monolayer (CS monolayer) which is isoelectronic to phosphorene [16] and its possible control under external strain.

In two-dimensional systems, strain can be applied indirectly by using thermal variations of the substrate [9] or directly by mechanical deformations [17, 18]. Theoretical studies predict that most 2D materials can tolerate strain values above 10% without ruptures [9, 18, 19]. For example, the graphene monolayers can easily tolerate strain above 25% [20]. Our aim is to provide a general picture of the connection between electronic and thermoelectric properties upon external strain, highlighting the efficiency of the strain applied in certain directions to control the bandgap.

Herein, we employ first-principles calculations to study the electronic and thermoelectric response upon strain for the carbon sulfide monolayers. Calculations show that the CS monolayer is a semiconductor stable at room temperature with an indirect bandgap [16]. Its structure is composed by single layer with two-dimensional honeycomb puckered structure where each atom is bonded to three neighbors. Because the CS monolayer has a structure similar to phosphorene, therefore we anticipate a similar improvement in mechanical flexibility [21] and highly anisotropic electronic properties [15].

2. Methodology

Density functional theory calculations were performed using the plane-wave self-consistent field plane-wave implemented in the QUANTUM ESPRESSO package [22] with the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE)
The group velocity of the state labeled with $\mathbf{k}$ is independent of the relaxation time. The constant relaxation time approximation (RTA), as implemented in the boltztrap code [28], has been successfully used to describe the transport coefficients of a wide range of thermoelectric materials [29–32]. In this approximation, the relaxation time is a constant and therefore the thermopower or Seebeck coefficient $S$ can be expressed as [28, 33],
\[
S = \frac{\hbar}{\sigma} \int d\varepsilon \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \Xi(\varepsilon) \frac{\varepsilon - \mu}{k_B T},
\]
where $\sigma$ is the scalar conductivity, $\varepsilon$ is the energy, $f_0$ is the Fermi distribution, $\mu$ is the chemical potential, $\hbar$ is the reduced Planck constant, $k_B$ is the Boltzmann constant, and $T$ is the temperature.

The Seebeck coefficient at the temperature $T$ and chemical potential $\mu$ can be expressed as [28, 33],
\[
S = \frac{\hbar}{\sigma} \int d\varepsilon \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \Xi(\varepsilon) \frac{\varepsilon - \mu}{k_B T},
\]
being the scalar conductivity $\sigma$ defined by
\[
\sigma = q^2 \int d\varepsilon \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \Xi(\varepsilon),
\]
with the transport distribution $\Xi$ defined as
\[
\Xi = \sum_k \tilde{v}_k \tilde{v}_k^* \tau_k,
\]
where $q$ is the carrier charge, $f_0$ the Fermi distribution, $\hbar$ the Boltzmann constant, $\tau_k = \tau_0$ the constant relaxation time and $\tilde{v}_k = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial \mathbf{k}}$ the group velocity of the state labeled with $\mathbf{k}$.

### 3. Results and discussion

Figure 1 shows the most stable CS monolayer structure, corresponding to a hexagonal structure with puckered sheets of bounded atoms in the same way as phosphorene. Similar structures can be found in group IV monochalcogenides (for instance GeSe, GeS, SnSe, SnS) [34–36], and group V semiconductors (PN or AsN) [37–39]. Each sulfur atom on the CS monolayer is bonded to three carbon atoms and vice versa [38]. The relaxed in-plane lattice vectors are $a = 4.03$ Å and $b = 2.77$ Å.

The band structure of the carbon sulfide layer in figure 2 reveals a semiconductor with an indirect bandgap of 1.1 eV, in agreement with the previous works [16]. Slightly higher than the 0.92 eV bandgap found for phosphorene [27, 40, 41]. The occupied bands below the Fermi level have a dominant

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1 For carbon, sulfur and phosphorus we use the pseudopotentials C.pbe-n-kjpaw.psl.0.1.UPF, S.pbe-n-kjpaw.psl.0.1.UPF and P.pbe-n-kjpaw.psl.0.1.UPF from the QUANTUM ESPRESSO pseudopotential data base: www.quantum-espresso.org/pseudopotentials.
contribution of $p$-orbitals from carbon atoms. Underneath these bands, a particular feature of the CS monolayer is the second bandgap located $\approx 3$ eV below the Fermi level. Followed by bands composed by $p$-orbitals from sulfur atoms.

We consider two uniaxial strain cases corresponding to modifications of the unit cell in the armchair and zigzag directions, and a biaxial case corresponding to a combination of tensile strain in both armchair and zigzag directions. The strain is introduced by changing the size of the lattice vector in the selected directions and then the structure is fully relaxed. Similar to molybdenite (MoS$_2$) [42], we find that the bandgap of the CS monolayer decreases as the tensile strain increases. This tendency is the opposite to that commonly observed in graphene, phosphorene and group-IV monochalcogenides monolayers [43–45].

For uniaxial strain along the armchair-direction (parallel to $x$-axis) in figure 3(a), the band structure is modified marginally. As the uniaxial tension in armchair-direction increases, the bottom of the conduction band at the high symmetry $Y$-point moves down and for a strain of 10% reaches the same level of the $\Gamma$-point. The bandgap of the CS monolayer is more sensitive to the uniaxial strain applied along the zigzag-direction (parallel to $y$-axis) as shown in figure 3(b). Contrary to the previous case, the gap closes even for small values of strain and the bottom (top) of the conduction (valence) band moves away from the high-symmetry points. In the figure 3(c), we can observe that the band structure upon biaxial strain ($x$ and $y$ direction simultaneously) shows a behavior similar to the uniaxial case applying strain in the zigzag direction. As the strain increases, the carbon $p$-bands move upward in energy producing several anticrossings near the Fermi level. For strain values of 10%, the HOMO-LUMO gap has completely disappeared and the transition between semiconductor and metal is complete. Note that, the second gap remains practically constant due to the almost rigid movement of the sulfur $p$-bands.

Employing the calculated electronic band structure as input, the transport coefficients are calculate using the Boltzmann transport theory within the constant relaxation time approximation. It is possible to correlate features from band structure with some aspects shown by the Seebeck coefficient $S$. Because electrons and holes contribute to the transport properties, the maximum of the Seebeck coefficient appears in the band gap [46, 47] and therefore it can be controlled with strain engineering.

In our calculations the maximum Seebeck coefficient around the Fermi level $S_{\text{max}}$ at room temperature (300 K) for the non-strained CS monolayer is 2.62 mV K$^{-1}$. Under the same conditions, for the phosphorene layer we find a $S_{\text{max}} = 2.16$ mV K$^{-1}$, in agreement with previous DFT-PBE calculations [27]. Note that hereafter we refer to $S_{\text{max}}$ as maximum Seebeck coefficient around the Fermi level. A second peak also appears in the Seebeck coefficient of the CS monolayer due to the second gap. We will not discuss it, because under normal experimental conditions it would be difficult to reach the level of doping necessary to be measured.

In figure 4, we present the room temperature Seebeck coefficient as a function of chemical potential for the CS monolayer under uniaxial strain in armchair-direction (a) and zigzag-direction (b), and biaxial strain in (c). The different colors are for different strain values. The inset shows the behavior around the $S_{\text{max}}$ for the strain applied along armchair-direction (parallel to $x$).
strain along the armchair-direction is minor, figure 4(a). This result can be expected from the small variations observed in the band structure upon uniaxial strain along that direction in figure 3(a).

Transport coefficients are easily controlled by strain in the zigzag direction. In figure 4(b) we can note how the behavior of the Seebeck coefficient against the chemical potential tends to a constant as the strain increases. For negative strain values corresponding to a compression of the system, we observe a large increase in the maximum value of the Seebeck coefficient. Both behaviors can be explained by the variation of the gap with the strain [10].

Given the response of the band structure to strain, the behavior of the Seebeck coefficient in case of biaxial strain is similar to that of the previous case. In figure 4(c), for positive strain values, the Seebeck coefficient follows the same trends of the uniaxial in zigzag-direction but with slightly lower values. The difference between both cases appears when considering the structural compression, the response of the Seebeck coefficient is smaller in the biaxial case.

The maximum Seebeck coefficient decays exponentially with the temperature without modifying the behavior described above. It is possible to follow the behavior of the maximum Seebeck coefficient value $S_{\text{max}}$ for a given temperature. On the one hand, the biaxial case is more susceptible to modifications to the positive strain values (corresponding to an expansion) where $S_{\text{max}}$ rapidly tends to zero, the strain in the zigzag direction $S_{\text{max}}$ follows the same trends, and the strain in the armchair direction only produces marginal effects in $S_{\text{max}}$. On the other hand, when considering negative strain values (corresponding to a compression) in the zigzag direction at room temperature and $-5\%$ strain the $S_{\text{max}}$ increases to 3.9 mV K$^{-1}$, the biaxial strain case produces a slight increase of $S_{\text{max}}$ to 3.1 mV K$^{-1}$, and contrary to these two, the strain in armchair direction produces a reduction of $S_{\text{max}}$ to 2.38 mV K$^{-1}$. As a reference, at 300 K for the non-strained case we find a $S_{\text{max}} = 2.62$ mV K$^{-1}$.

As previously noted, the electronic and thermoelectric responses of the CS monolayer are contrary to that observed in graphene and phosphorene layers [44, 45]. Taking advantage of the fact that the Seebeck coefficient is low for conductors and the electronic conductance tends to be low for insulators [7]. Devices could be designed taking advantage of inhomogeneous response upon strain using heterojunctions or controlled stacking to obtain a strain-dependent thermal and electronic responses [5, 8, 48–51].

### 4. Final remarks

The bulk carbon–sulfur compound was synthesized by forcing the reaction of sulfur with carbonized charcoals at high temperatures [52, 53]. The isolation of the carbon sulfide monolayer could be achieved thought the mechanical exfoliation of bulk material [54]. Another possible method to synthesize the CS monolayers is to perform a chemical vapor deposition (CVD) process using appropriate carbon and sulfur compounds as precursors [55]. The precursors would react in a furnace at high temperatures, resulting in the formation of CS monolayers on a suitable substrate. The fine adjustment of the growth parameters would control the number of layers and the appearance of the different structural phases. However, specific details of the procedures are beyond the scope of the present work. We expect that this work will encourage experimental groups to synthesize carbon sulfide monolayers.

In conclusion, we have investigated the strain response on the electronic and thermoelectric properties of carbon sulfide monolayer based on the PBE-DFT calculations combined with the semiclassical Boltzmann theory. We found a highly anisotropic electronic and thermoelastic response upon strain. When the strain is applied in the armchair direction, the bandgap and Seebeck coefficient remain almost unchanged. In contrast, when strain is applied in the zigzag direction the Seebeck coefficient is easily modulated, going from a finite value to zero with relatively small strain values. By tracking the evolution of the Seebeck coefficient as a function of external strain we can follow the change in bandgap induced by the strain. Our results suggest possible applications as sensors or active component taking advantage of the real-time bandgap modulation.

### Acknowledgments

The author gratefully acknowledges the critical reading of the manuscript and the suggestions made by L. Chico and S. Sadewasser.

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