

Remarkable suppression of thermal conductivity by point defects in MoS₂ nanoribbons



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ABSTRACT

By applying non-equilibrium molecular dynamics simulation, we investigate the effect of point defects on thermal conductivity of MoS₂ nanoribbons, such as sulfur vacancies (V_S) and oxygen substitutions to sulfur (S_O). It is found that both V_S and S_O can significantly reduce thermal conductivity of monolayer MoS₂ nanoribbons, but the suppression of thermal conductivity by vacancies is stronger than that by substitutions. For armchair MoS₂ nanoribbon of 41.1 nm length and 4.4 nm width, when defect density is only 1.5%, the reduction of thermal conductivity at room temperature by V_S defects and S_O defects is 42.3% and 35.1%, respectively. We perform the vibrational eigenmodes analysis and find that the strong localization of phonons of all modes by defects results in the severe reduction of thermal conductivity of MoS₂ nanoribbons. Further spectra analysis reveals that the localized modes are located in the sites of defects and the sites around defects, due to the change of force constant at these sites. Our findings are helpful for understanding and tuning the thermal conductivity of MoS₂ nanoribbons by defect engineering.

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1. Introduction

One of the promising approaches for solving the energy crisis is thermoelectric material [1–5]. The performance efficiency of thermoelectric materials is best measured by the figure of merit: $ZT = S^2 \sigma T / \kappa$, where S is the Seebeck coefficient, T is the absolute temperature, σ is the electrical conductivity, and κ is the total thermal conductivity, respectively. Unlike the superior thermal conductivity of graphene [6–9], the thermal conductivity of monolayer MoS₂ is low, which has been presented by theoretical analysis [10–15] and experimental measurements [16]. Very recently, a large value of thermoelectric Seebeck coefficient for monolayer MoS₂ was observed experimentally [17]. The large Seebeck coefficient and low thermal conductivity suggest potential thermoelectric applications of 2D MoS₂ [18]. It is still necessary to reduce the thermal conductivity of monolayer MoS₂ for higher thermoelectric performance. Due to spatial confinement of acoustic phonons and significant change of phonon mean free path (MFP), size and edge roughness effects are applied to modulate the thermal conductivity of low-dimensional materials, such as silicon nanowires and graphene nanoribbons. However, these strategies are disabled to effectively engineer the thermal conductivity of

monolayer MoS₂, because the thermal conductivity of monolayer MoS₂ is size and roughness insensitive, which results from the ultra-short phonon MFP (about 14.6 nm at room temperature) [13]. Another approach to remarkably suppress the thermal conductivity is phonon-point defect scattering, such as isotope, vacancy, and substitution. Although systematic investigations of point effects on thermal conductivity of graphene have been performed [19–23], these knowledge of monolayer MoS₂ are scarce so far. In this work, non-equilibrium molecular dynamics (NEMD) simulation is performed to present the significant reduction of thermal conductivity of MoS₂ nanoribbons by defects of sulfur vacancy, as well as oxygen substitution to sulfur. Furthermore, we perform the vibrational eigenmodes analysis and evaluate the spatial distribution of localized modes to demonstrate that the strong localization of phonons near the defects suppresses thermal transport greatly and is responsible for the significant reduction of thermal conductivity.

2. Models and simulation methods

Fig. 1(a) gives the structure of monolayer MoS₂, the atoms in yellow are sulfur and the atoms in cyan are molybdenum. The lattice parameter of unit cell is 3.16 Å, which is from the experimental data [24], and the effective layer thickness is 4.41 Å [25]. The monolayer MoS₂ nanoribbon along the armchair direction is built firstly. Then sulfur atoms are randomly deleted to form vacancy defects or substituted by oxygen atoms. In all types of vacancy, only mono-sulfur vacancy (V_S) is considered, because V_S is found to have the

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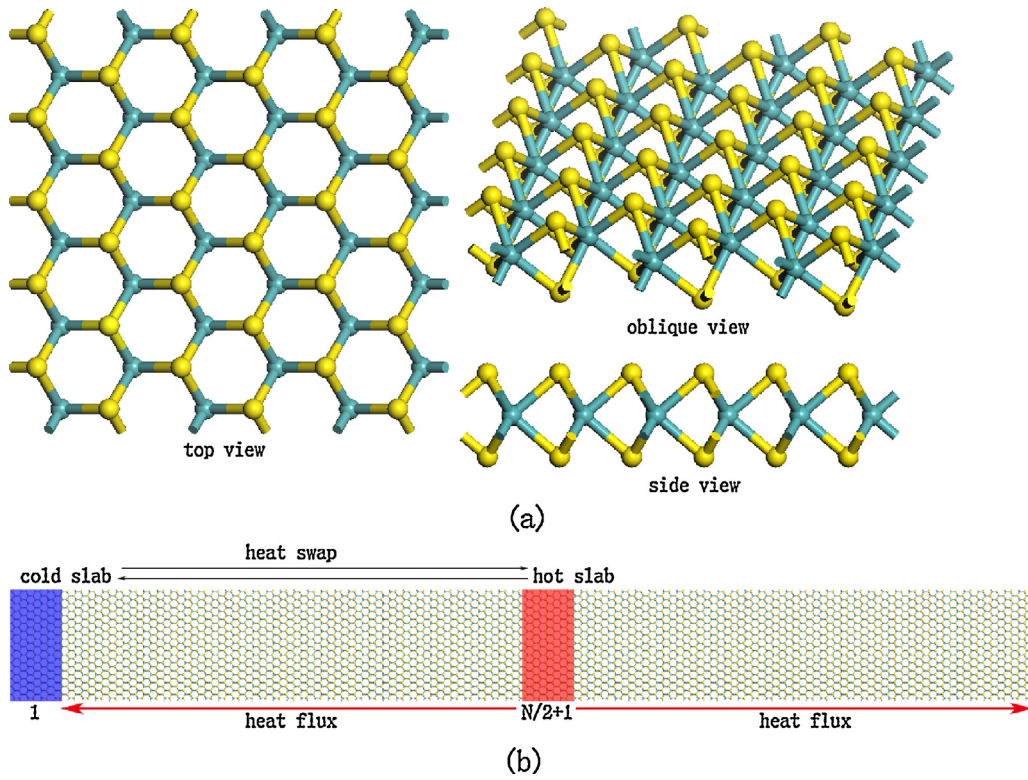


Fig. 1. (a) The structure of monolayer MoS₂: top view, oblique view, and side view. The atoms in yellow are sulfur and the atoms in cyan are molybdenum. (b) Schematic illustration of simulation model in the Müller-Plathe method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

lowest formation energy, and is frequently observed in samples of experiment [26]. Because it has been proposed that oxygen could be substituted for sulfur in individual MoS₂ crystal lattices on the basis of a qualitative molecular orbital model [27], we research the effect of oxygen substitution to sulfur (S_O) on thermal conductivity of MoS₂ nanoribbons.

The code LAMMPS [28] is applied to carry out the molecular dynamics simulation, and the thermal conductivity of monolayer defective MoS₂ nanoribbons along armchair direction is calculated by Müller-Plathe (MP) [29] method as illustrated in Fig. 1(b). The periodic boundary condition is used in longitudinal direction of nanoribbons. The simulation box is subdivided into N (N must be an even number) slabs along the longitudinal direction. Slab 1 is defined as the cold slab and slab $N/2 + 1$ as the hot slab. Based on MP method, the hottest atom with maximal kinetic energy in the cold slab and the coldest atom with minimal kinetic energy in the hot slab are identified, and the velocity components in the Cartesian coordinate system of these two atoms are interchanged, if the kinetic energy of the hottest atom in the cold slab is higher than that of the coldest atom in the hot slab. Energy is made to be transferred artificially from the cold to the hot slab in this manner, and temperature gradient along the longitudinal direction is established. The thermal conductivity of nanoribbon can be calculated by the following equation,

$$K = \frac{Q}{2At(\partial T/\partial x)} \quad (1)$$

where, Q is the summation of energy interchanged in the simulation, A is the cross-sectional area of nanoribbon, t is the time of the simulation, and $\partial T/\partial x$ is the gradient of temperature in the longitudinal direction. The factor 2 arises because of the periodic boundary condition of the system in the longitudinal direction.

The Stillinger–Weber [30] potential is used, and the potential parameters to describe the interatomic interactions within monolayer MoS₂ origin from Ref. [31], which are fitted to an experimentally obtained phonon spectrum of monolayer MoS₂, and provide a good description for the energy gap and the crossover in the phonon spectrum. The temperature in all simulation is 300 K (room temperature). The time step of MD simulation is 0.5 fs. The system is firstly equilibrated in the isothermal–isobaric ensemble (NPT) for 5 ns. After the NPT relaxation, we continue to relax the system in the microcanonical ensemble (NVE) for 1 ns. In order to establish a temperature gradient along the longitudinal direction, the MP method is adopted and the NEMD is performed for 3 ns. The simulation of final 2 ns is to calculate the thermal conductivity of nanoribbon by Eq. (1). For each of defects concentration, the results are averaged over 20 simulations to reduce the fluctuation.

3. Simulation results and discussions

As shown in Fig. 2(a), the thermal conductivity of monolayer MoS₂ nanoribbons decreases with increasing density of defects. Both V_S and S_O can significantly reduce the thermal conductivity of monolayer MoS₂ nanoribbons, but the suppression of thermal conductivity by vacancies is stronger than that by substitutions. For example, with defect density as 1.5%, the reduction of thermal conductivity by V_S defects and S_O defects is 42.3% and 35.1%, respectively, for armchair MoS₂ nanoribbon of 41.1 nm length and 4.4 nm width. Fig. 2(b) gives the linear relationship between the reciprocal of thermal conductivity and the density of defects.

In kinetic theory, thermal resistivity is the reciprocal of thermal conductivity, and it is expressed by

$$\kappa^{-1} \propto C^{-1}v^{-1}l^{-1} \quad (2)$$

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