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Communication

# Van der Waals bilayer antimonene: A promising thermophotovoltaic cell material with 31% energy conversion efficiency

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ABSTRACT

Antimonene has recently been theoretically predicted and experimentally demonstrated as a new type of two-dimensional (2D) material with high stability and promising potential for optoelectronic applications. However, it is still a significant and open issue to harvest electromagnetic wave radiation as much as possible and convert it into electricity via antimonene. Here, for the first time, we propose a van der Waals (vdW) stacking strategy of antimonene for thermophotovoltaic (TPV) cells, which could achieve radiation-to-electricity efficiency as high as 31%, exceeding the traditional TPV materials such as Ge and GaSb. The vdW bilayer and trilayer antimonenes with high thermodynamic stability were constructed according to density functional theory (DFT). Surprisingly, among them, the AC-stacking vdW bilayer antimonene exhibited a bandgap of 0.62 eV via Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) containing spin-orbital coupling (SOC), falling into the optimum range of the TPV requirement (0.35–0.75 eV). Such a decisive advantage enables the AC-stacking vdW bilayer antimonene to be a very promising material for high-efficient TPV cell, which has been evidenced by an energy conversion efficiency of 31% for the foremost designed vdW bilayer Sb/AC-based TPV. The concept reported here associated with the recent experimental progress on vdW multilayer antimonene could open the door of high-efficient TPV devices based on 2D materials.

## 1. Introduction

Since the report of antimonene in 2015 [1–3] and its subsequent derivatives [4–9], such freestanding two-dimensional (2D) semiconductors on theoretical predication have been widely studied and regarded as promising materials for various device applications. In particular, few-layer antimonenes via mechanical isolation [10], liquid-phase exfoliation [11], and van der Waals (vdW) epitaxy growth [12] have been experimentally prepared recently. These experimental achievements will lead to a surge of interests in 2D vdW antimonene, namely the layered grey antimony with the constructing foundations of 2D thin sheets bonded together by weak vdW interaction [13]. Moreover, the multilayer vdW antimonene nanoribbons (not natural AB-stacking) with an opening band gap were successfully fabricated by the plasma-assisted process recently [14]. Thus, stacking different patterns of 2D vdW atomically thin antimonene together bring in unique properties that range from semimetallic to semiconducting material and applications in optoelectronic device such as thermophotovoltaic (TPV) cells.

It has been known that the TPV cell can directly convert a thermal emission from a high-temperature emitter into electric power [15]. In comparison to solar photovoltaic, TPV has a crucial merit: its conversion is suitable for any high-temperature heat source, incl. the combustion, nuclear, solar and waste heat sources [16]. It has been a significant worldwide concern regarding how to reutilize such high temperature radiation energy. At present, for a workable high-temperature radiator ($T_e \leq 2000$ K), the bandgap of the active material in TPV should satisfy $E_g \leq 1.0$ eV. Although great improvements have been achieved, a narrow bandgap (especially from 0.35 to 0.75 eV) [17] cell is still urgently needed to meet the requirement for a high efficiency TPV device.

In this work, we find that a vdW bilayer grey antimony (not AB stacking) with high conversion efficiency applied in the TPV device. Based on the density functional theory (DFT), various 2D stacking types for vdW bilayer and trilayer grey antimony are investigated. They have been verified to be dynamically stable based on phonon spectra analysis and molecular dynamic simulation. Interestingly, AA- and AC-stacking vdW bilayers have nonzero bandgap, which are entirely

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different from AB-stacking vdW bilayer antimonene and trilayers with zero bandgap. Particularly, AC-stacking vdW bilayer antimonene has a narrow bandgap of 0.62 eV, which perfectly fulfill the required optimum absorption range for TPV cell. This advantage enables vdW bilayer Sb/AC to be a potential candidate as photon-absorbing material for high efficiency TPV device. The theoretical calculations demonstrate a considerably high conversion efficiency of 31% of the vdW Sb/AC-based TPV cell. Due to the predicted high conversion efficiency, we believe that vdW Sb/AC-based device has the potential to be realized as environmental friendly TPV cell.

## 2. Computational methods

For the different stacking vdW bilayer and trilayer grey antimony, the numerical calculations have been employed with first-principles DFT, using the Vienna Ab initio Simulation Package (VASP) [18,19]. Projector-augmented-wave (PAW) methods [20] for Sb atom were applied to understand the electrostatic interactions between valence and core electrons. The atomic optimization and electronic structure calculations were performed under Generalized Gradient Approximation (GGA) [21] of Perdew, Burke, and Ernzerhof (PBE) [22] functional. For the calculations of electronic structures, we also implemented Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [23,24] to correct the underestimated bandgaps at PBE functional. The Monkhorst-Pack [25] was used for the *k*-point sampling, and we applied 21 × 21 × 1 and 7 × 7 × 1 Γ-centered meshes for the PBE and HSE06 functionals, respectively. The vdW [26,27] interaction between the layers was performed using Grimme's (DFT-D2) [28] correction to our functionals. Plane-wave cutoff energy of 500 eV was applied. The convergence criterion of the self-consistent field calculations was set to $10^{-5}$ eV for the total energy. Regarding the artificial interlayer interaction, 20 Å thick vacuum layer was used. The atomic positions were fully optimized until the Hellmann–Feynman forces on all atoms were less than 0.005 eV/Å.

To assess the kinetic stability of AC-stacking vdW bilayer grey antimony, phonon band dispersions were calculated by using the Cambridge Sequential Total Energy Package (CASTEP) [29], where 13 × 13 × 1 k mesh was used. First-principles molecular dynamic simulations using PAW method and PBE functional were carried out to evaluate the thermal stability of all the predicted AC-stacking vdW bilayer grey antimony. In the molecular dynamics simulations, the initial configurations of AC-stacking vdW bilayer grey antimony with 4 × 4 supercell (64 Sb atoms) was annealed at 300, 600 and 900 K, and each molecular dynamics simulation in NVT ensemble lasted for 5.0 ps with a time step of 2.0 fs. The temperature was controlled by the Nosé-Hoover method [30]. Moreover, for the $H_2O$ reaction with AC-stacking vdW bilayer grey antimony (4 × 4 supercell), we adopted the same method with that in room temperature.

Based on our rational device and detailed balance principle, the energy conversion efficiency $\eta$ of a vdW Sb/AC-based TPV device can be defined as [31]

$$\eta = x_g \int_{x_g}^{\infty} \frac{x^2}{e^x - 1} dx / \int_0^{\infty} \frac{x^3}{e^x - 1} dx, \quad (1)$$

here $x_g$ is given by:

$$x_g = qE_g/kT_e, \quad (2)$$

where $E_g$ is the bandgap of the TPV cell (vdW Sb/AC), $q$ is elementary charge ($q$ = 1.60×10$^{-19}$ C), $k$ is Boltzmann constant ($k$ = 1.38 × 10$^{-23}$ J K$^{-1}$) and $T_e$ ($T_e$ = 1800 K) is the temperature of emitter. For simplicity, we ignore the series, parallel resistance and surface reflection losses.

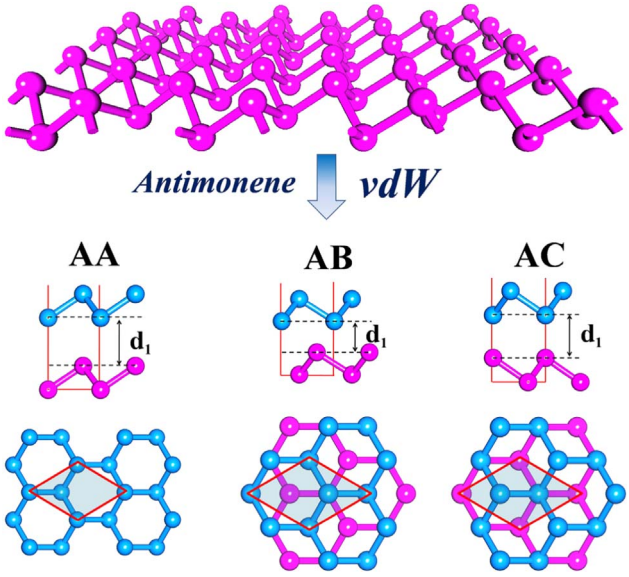


**Fig. 1.** Schematic diagram of antimonene changing into bilayer grey antimony by vdW interaction. Side and top views of three stacked (AA, AB, and AC) vdW bilayer grey antimony (lower panel). $d_1$ represents the interlayer distance. The red lines in the bottom panels represent the rhombus primitive cell.

## 3. Results and discussion

### 3.1. Models of antimonene bilayers

The schematic structures of monolayer antimonene can change into bilayer and trilayer grey antimony by vdW forces (Figs. 1 and S1). The possible stacking patterns for vdW bilayer and trilayer grey antimony are also presented, among which AB (bilayer) and ABC (trilayer) stackings are the ground state structures [1]. To obtain these vdW stacking patterns, individual monolayers are transferred based on the AB and ABC-stacking ground states [1]. For example, AA stacking can be realized by transferring two-thirds and one-third of the unit cell along both a and b directions of the bottom layer of AB-stacked vdW bilayer antimonene, respectively.

The relaxed lattice constants (a = b) of vdW bilayers and trilayers are listed in Tables S1 and S2. The distinguished difference among the different stacking forms is the interlayer distance between individual layers. It increases from 2.57 Å in AB stacking to 3.49 Å in AA stacking, and further to 4.99 Å in AC stacking. The interlayer distance is inversely proportional to the binding energy in vdW bilayers. Meanwhile, the AA- and AC-stacking vdW bilayers show low stability (still no soft modes in phonon spectra as illustrated by analysis later) as a result of the competition between electrostatic interactions and vdW, indicating a larger repulsive force between the two layers. This is usually related to stronger Pauli repulsions, caused by a more pronounced overlap of electron densities (steric effect). For vdW trilayers, except for AAA and ABC stackings exhibiting two equivalent interlayer distances, the remaining seven stackings possess two quite different interlayer distances. It is noteworthy that AAC and ACC stackings are the same structure.

Notably, the most stable stacking is ABC, which is the same as the bulk grey antimony. The related parameters about vdW trilayers are listed in Table S2.

### 3.2. Stability of antimonene bilayers

Stability is a primary concern for realizing practical applications of the theoretical designed materials [32–37]. The stabilities of vdW bilayers and trilayers are confirmed via phonon spectra, binding energy and molecular dynamic calculations. Considering that no soft modes