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THERMIONIC DEVICE WITH GRAPHENE ELECTRODES

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In this paper, we propose van der Waals heterostructure-based thermionic devices for the applications in cooling and power generation in the temperature range of 300 to 400 K. By using two-dimensional materials of low cross-plane thermal conductivity as the barrier materials and graphene as electrodes, our calculation demonstrates that our proposed device will have a higher efficiency as compared to other methods such as thermoelectric device and the traditional thermionic devices. By using the parameters within the current technology, we predict a cooling capability at more than 50% of the Carnot efficiency, and a 10 to 20 % efficiency in harvesting the wasted heat at 400 K.

KEYWORDS : Thermionic emission, cooling, power generation, van der Waals Heterostructure

INTRODUCTION

Thermoelectric devices, in which electrons function as heat steam in the engines or cooling fluid in the vapor-compressor of refrigerators, can realize direct heat conversion into electricity, respectively, for heating and cooling, simply by controlling the direction of the electron current. Currently, practical applications have been limited to specific areas by considering factors such as size, maintenance and fast response time, instead of efficiency [1]. Similar to the thermoelectric devices, thermionic devices operate on same principle. When current flows toward the cold side, it is a refrigerator. In reverse direction, it becomes an energy harvesting device of converting the waste heat to electricity directly.

In the traditional thermionic device of cathode-vacuum (or gas) - anode configuration, it cannot work at room temperature due to the high work function of cathode materials. To operate at room temperature, the work function is required to be below 0.34 eV [2].

Consequently, Schottky contact can be utilized to produce different barrier height (0 to 0.4 eV), rendering thermionic devices workable at room temperature [3–5]. The original multilayer heterostructure with multiple barriers based thermionic device [4] is, however, limited by very small temperature drop of single barrier (around 1 K) due to the high thermal conductivity of the traditional semiconductor used. This problem may be able to be solved by using two-dimensional (2D) atomic crystal layers of ultralow thermal conductivity, such as graphene and other 2D atomic-thickness materials [6–10].

These atomic layer materials can be stacked into heterostructures, so-called the van der Waals (vdW) heterostructure [11] due to week vdW bond between the layers. Experimental and theoretical investigations of these artificial layered crystals reveal unusual electronic and thermal properties [12–14], such as ultrafast charge transfer [15], and ultralow cross-plane

thermal conductivity [16, 17], etc. Electronic and optoelectronic devices based on these materials are predicated to out perform the conventional bulk materials.

We are interested in exploiting vDW heterostructues to design a room-temperature solid-state thermionic device (cooler and power generator) based on the unique and excellent properties of 2-D materials, as shown in the Fig. 1. From our model and calculated results, we identify the required parameters of achieving high-efficiency performance. It is fount that our proposed devices are better than existing devices, if an optimal combination of reassembling different two dimensional atomic layers is achieved. In particular, it can be a power generator to harvest low-grade waste heat (< 400 K) with a maximum efficiency of about 24%.

Thermionic cooling and power generation operate on the principle of thermionic emission from metal or semiconductor, and it is governed by the well-known Richardson-Dushmann (RD) equation, $J\ (\phi, T) = AT^2 \exp\ (-\ e\phi/k_BT)$, where $A = emk_B^2/2\pi^2\hbar^3$ is the Richardson constant, e is the electron charge, m is the effective electron mass, k_B is the Boltzmann constant, and $\hbar$ is the reduced plank constant. Due to the unique linear band structure and finite density of state of single layer graphene, our recent work [18] shows that thermionic emission from a single suspended graphene monolayer is governed by a new scaling law, $J\left(\phi, T, E_F\right) = A^* T^3 \exp\left(-\left(e\phi - E_F\right)/k_BT\right)$ where $A^* - ek_B^3/\pi\hbar^3 v_f^2 = \quad 0.1158\,\text{A/cm}^2/\text{K}^3, v_f$ is the Fermi velocity, E_F is the Fermi level and ϕ is the work function of graphene.

Methods

In Fig. 1, we model the vdW-based thermionic device which utilizes multiple graphene layers as multiple electrodes between the hot and cold side. There is a fixed and constant barrier height between the two electrodes without applied bias. With an applied voltage of V, the Fermi level in the right graphene (anode) is lowered, and potential barrier becomes a trapezoid profile. The electric current (J_e) and heat current (J_Q) through the sandwiched structure are, respectively,

$$J_e - J_{G_C} - J_{Gh}\, e^{-\frac{eV}{k_BT_h}}, \qquad \ldots (1)$$

$$J_Q = \left(\phi' + \frac{3k_BT_c}{e}\right) - \left(\phi' + \frac{3k_BT_h}{e}\right) J_{Gh}\, e^{-\frac{eV}{k_BT_h}}, - \frac{T_h - T_c}{R} \qquad \ldots (2)$$

Here, $J_{Gi} = AT_i^3 \exp\left(-\left(e\phi'\right)/k_BT_i\right)$ is the thermionic current density over an effective Schottky barrier height of ϕ' $\left(\phi' = \phi = E_F\right)$ formed at the interface between graphene and vdW, where the labelling $i = c$ and $i = h$ denote the electrode of cold and hot side, respectively. Note ϕ' can be tuned via varying E_F of graphene through chemical or electrostatic doping. The second term of Eq. (2), 3 k_BT measures the average heat energy per emitted electron, which can be obtained through the internal energy of electron in graphene associated with one degree of freedom, $U = k_BT^2\left(\frac{d\ln\left(\Xi\right)\left(k\right)\right)}{dT}\right)$, with $\Xi\left(k\right)$ being partition function. In the last term of Eq. (2), R is the thermal resistance (per area), including effects due to interface, barrier layer and electrode. In general, if R is mainly due to barrier layer, we have $R \propto k^{-1}$, which decreases

with the thickness of the barrier (d), unless the cross-plane thermal conductivity (k) can be reduced at small d.

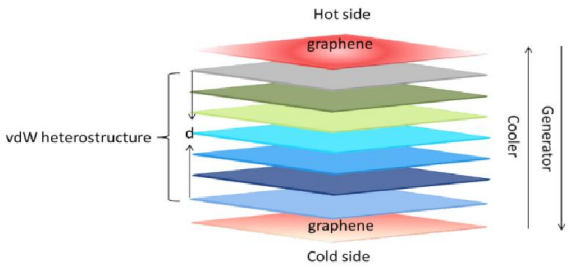

Fig. 1 : Schematic diagram of van der Waals heterostructure-based solid state thermionic device with graphene electrode. where *d* is the thickness of van der Waals heterostructure.

By defining the average temperature as $T = (T_h + T_c)/2$, and the temperature difference as $\delta T = T_h - T_c$, in the limit of $T \ll T$ and eV $\ll k_B T$, Eqs. (1) and (2) become

$$J_e = J_G\left(\frac{eV}{k_B T} - (\alpha+3)\frac{\delta T}{T}\right), \quad \ldots (3)$$

$$J_Q = J_G(\alpha+3)\frac{k_B T}{e}\left(\frac{eV}{k_B T} - (\alpha+3+\beta)\frac{\delta T}{T}\right), \quad \ldots (4)$$

where $\alpha = \frac{e\phi'}{k_B T}, \beta = \frac{\gamma+2}{\alpha+3}, \gamma = \left(\frac{T_R}{T}\right)^3 e^{\alpha}$, and $(k_B T_R)^3 = \frac{\pi\hbar^3 v_f^2}{k_B R}$; J_G is defined for mean temperature T. Here, we have introduced a temperature like dimensional constant T_R, which depends only the thermal conductivity κ and scales as $T_R \propto \kappa^{1/3}$.

To operate at cooling regime, we must have $J_Q > 0$, which poses a condition of

$$\frac{eV}{\alpha+3+\beta} > k_B \delta T. \quad \ldots (5)$$

The efficiency of the cooling is calculated by $\eta = J_Q / J_e V$ and its maximul value (η_{max}) is obtained by taking derivative with respect to applied voltage V:

$$\frac{\eta_{max}}{T/\delta T} = \frac{\alpha+3}{\left(\sqrt{\alpha+3+\beta}+\sqrt{\beta}\right)^{2,}} \quad \ldots (6)$$

which is a function of Schottky barrier height ϕ' and thermal resistance k (through T_R term embedded in β) for a given temperature set of T (or T_h and T_c). Note that the term $T/\delta T$ can be approximately regarded as the Carnot efficiency of cooling.

Results and discussion

In Fig. 2, we plot the maximum efficiency (in terms of the Carnot efficiency) or Eq. (6) as a function of $\phi' = 0$ to 0.5 volt for different T_R [K] = 300, 200, 100, 50, 1.7 at T_h = 300 K and T_c = 260 K (or $T = (T_h + T_c)/2$ = 280 K. It is clear that the normalized efficiency increases with small T_R, and it approaches the Carnot efficiency at the limit of $T_R/T << 1$. For a fixed T_R, there is an optimal value of ϕ' to have the maximal efficiency.

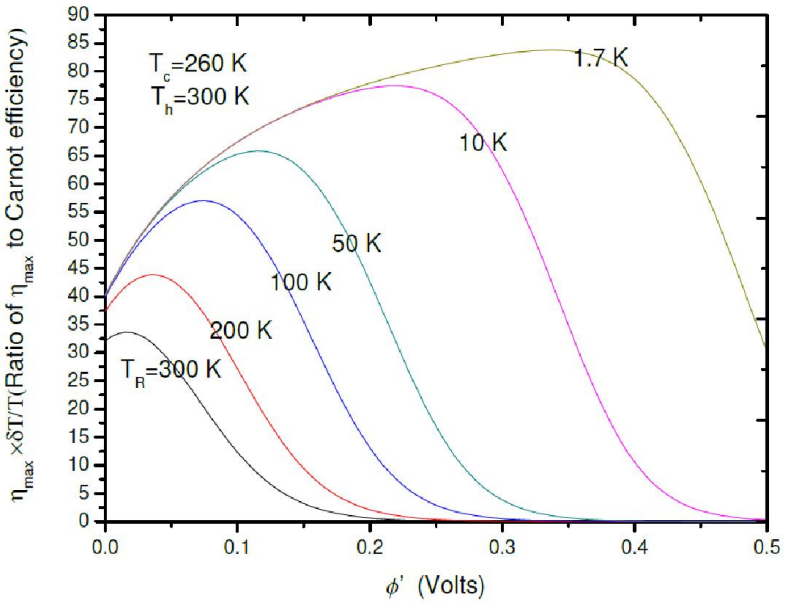

Fig. 2. The ratio of maximum cooling efficiency η_{max} to Carnot efficiency as a function of barrier height ϕ' at T_c = 260 K and T_h = 300 K for different TR [K] = 1.7, 10, 50, 100, 200 and 300.

In order to have very small TR, one can select two-dimensional (2D) materials of high thermal resistance R or low thermal conductivity k, such as 2D hexagonal Boron Nitride (h-BN) and transitional metal dichalcogenides (TMD) materials having very low cross-plane thermal conductivity [19] : κ = 0.05 W/mK for WSe_2 and κ = 0.1 to 1 W/m/K for MoS_2 [19]. Consider we can stack barrier alternatively by using WSe_2 and MoS_2 to form superlattice, we may achieve ultra-large interface thermal resistance due to acoustic mismatch between different materials. Taking WSe_2 for an example with a thermal resistance of R = 20 m^2 K/W, we may get 80% of Carnot efficiency, which corresponds to the T_R = 1.7 K as shown in Fig. 2. Compared with thermionic refrigeration based on the traditional configuration of metal-semiconductor-metal heterostructure [4], the efficiency of our proposed vdW heterostructure here is increased by more than 10%. For example, Fig. 2 shows a maximum efficiency is about 57% of the Carnot efficiency at T_R = 100 K, as compared to about 44% [4].

In comparison, the thermoelectric (TE) based cooler commercialized in some areas, such as air-conditioned car seats, and semiconductor laser cooling, has an efficiency of less than 7%. The low efficiency of the TE cooler is mainly limited by figure of merit ZT of the TE materials. Even with the highest reported value of ZT = 2.4 for Bi_2Te_3/Sb_2Te_3 superlattice structure [20], the efficiency is limited to 24.3% of Carnot efficiency at same T_c = 260 K and T_h = 300 K.

In practical applications, refrigerator has to pump a heat flux of up to few hundreds W/cm^2. For our proposed thermionic cooling device, the pumped heat current is approximately obtained by

$$J_Q \approx 3A_G T_c^2 \phi'(T_h - T_c) \times \exp\left(-\frac{e\phi'}{k_B T_c}\right) \quad \ldots (7)$$

where A_G = 0.01158A/cm^2/K^3. At T_c = 260 K, T_h = 300 K, T_R = 100 K, and ϕ' = 0.06 V, the estimated cooling power be up to 500 W/cm^2.

The proposed vdW heterostructure thermionic device can also be used for power generation for which the electrons flow from the hot cathode to the cold anode. Without the applied voltage, the electrons travelling over the Schottky barrier formed at the interface between graphene and vdW is by the thermionic emission, which results in a current flow via an external circuit to be extracted as thermionic power output. As stated in the introduction, the traditional cathode-vacuum-anode thermionic converter (TIC) is limited to the high-temperature operation (above 1500 K) to have an output current larger than 1 A/cm^2 due to the high work function of cathode. Here, we will show that our proposed vdW-TIC can harvest the waste heat at a much lower temperature (T_h = 400 K and T_c = 300 K) with a higher efficiency than the TE-based power generator.

The efficiency of our power generation is calculated by $J \times V/J_{Qh}$, which gives

$$\eta_g = \frac{\delta T}{T} \times \frac{\left(\sqrt{\alpha+3+\beta} - \sqrt{\beta}\right)^2}{(\alpha+3)}. \quad \ldots (8)$$

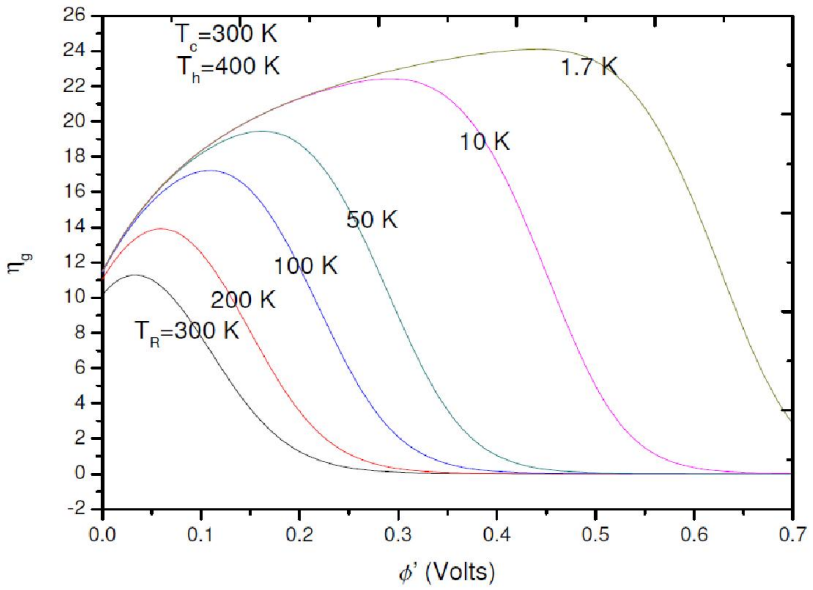

Fig. 3. The efficiency η_g for power generation as a function of barrier height ϕ' at T_c = 300 K and T_h = 400 K for different *TR* [*K*] =1.7, 10, 50, 100, 200, and 300.

The calculated results are plotted in Fig. 3 as a function of ϕ'' for TR [K] = 300, 200, 100, 50, 10 and 1.7 at fixed T_c = 300 K and T_h = 400 K. From the figure, we see that the efficiency of the solid-state vdW TIC is higher than 20% in the range of ϕ' = 0.2 to 0.4 V at T_R = 10 K. Even at higher T_R = 300 K and ϕ' = 0 to 0.1 V, we have η_g = 8 to 11%, which is better than some best power generators, such as a two-layer WSe_2 *TE* based system (ZT = 2.1) has a maximum efficiency of 7.6% at the room temperature, [19], and an electrochemical system for harvesting low-grade waste heat energy (< 100 ºC) has an efficiency of less than 8% [21]. Note the maximum theoretical efficiency is only about 9.5% at T_h = 400 K and very high $ZT = 4$ [22], by $\eta_{TE} = \frac{(T_h - T_c)}{T_h} \times \left(\frac{\left(\sqrt{1+ZT} - 1\right)}{\left(\sqrt{1+ZT} + T_c / Th\right)} \right)$.

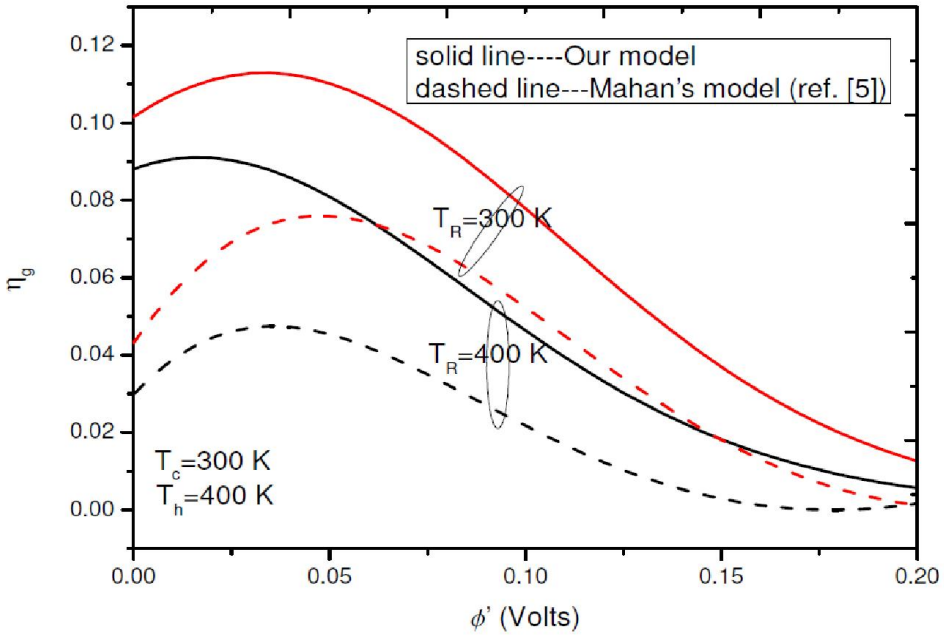

Fig. 4: A comparison of our model (solid lines) with Mahan's model (dashed lines - [5]) at T_c = 300 K and T_h = 400 K for T_R = 300 K and 400 K.

In Fig. 4, we compare the efficiency of our model in using graphene as the electrode and Mahan's model [5] in using conventional metals at T_R = 300 K and 400 K. It is clear that the graphene-based device has better efficiency than metal-based one due to the new thermionic emission mechanism of graphene [18].

It is worth to discuss briefly that the proposed parameters used in our model is within the capability of current technology and understanding. Just to state a few examples, single-layer graphene (to be used as electrodes) can be easily fabricated such as mechanical exfoliation [11], grown on the metal (e.g. copper) with the epitaxial method [23], and synthesized by chemical vapor deposition (CVD) methods [24]. Two dimensional materials (to be used as the barrier layer), such as MoS_2, h-BN, WS_2 and WSe_2, have been also isolated by mechanical exfoliation method. The stacking of isolated atomic layers of low-thermal-conductivity alternatively into van der Waals heterostructures has been shown [11].

First principle calculations [25] have demonstrated that the in-plane lattice thermal conductivity of monolayer TMD materials (*e.g*. MoS_2, $MoSe_2$ WS_2 and WSe_2) is about 0.1 to 0.3 W/m/K at temperatures of 100 to 400 K. Moreover, the cross-plane lattice thermal conductivity of single-layer TMD materials is predicted to be one order of magnitude lower than in-plane [16, 17, 26], and thus we will have *k* on order of 0.01 W/m/K, which implies that low values of $T_R < 100$ K proposed here is possible. The tunability of barrier height between the graphene and the barrier layer, ϕ' from 0 to 0.5 eV, is possible by tailoring the tailoring from Schottky contact to Ohmic contact [27, 28].

To achieve high efficiency predicted above, we need to ensure the transport of the electrons across the barrier layer is due to thermionic emission. Thus there is a minimum thickness *d* of the barrier required to prevent quantum tunneling, and *d* is estimated by using $d \approx \sqrt{\frac{e\phi'\hbar^2}{8k_B^2T^2m^*}}$, where *m** is the effective electron mass of the barrier layers [29], *e.g*. *m** = 0.6 m_e for MoS_2, 0.7 m_e for $MoSe_2$, 0.44 m_e for WS_2 and 0.53 m_e for WSe_2 (m_e is the electron mass).

Conclusion

In the present study of thermionic cooler and power generator based on van der Waals (vdW) heterostructure and using monolayer graphene as electrodes. The heterostructure is composed of two-dimensional materials of low cross-plane thermal conductivity. For both cooling and power generation, our calculations demonstrate that our proposed design is more efficient than currently used/proposed thermoelectric devices. The design parameters proposed here are within the reach of the current technology, and this device will be useful for various applications, such as thermal management of chip-based microelectronics [30-31].

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