Nano Energy 32 (2017) 67–72

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Back-gated graphene anode for more efficient thermionic energy converters

Hongyuan Yuan[a,*], Daniel C. Riley[a], Zhi-Xun Shen[a,e], Piero A. Pianetta[b,d], Nicholas A. Melosh[c], Roger T. Howe[b,*]

[a] Department of Physics, Stanford University, CA 94305, United States
[b] Department of Electrical Engineering, CA 94305, United States
[c] Department of Material Science and Engineering, Stanford, CA 94305, United States
[d] Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, MS31, Menlo Park, CA 94205, United States
[e] Department of Applied Physics, Stanford, CA 94305, United States

ARTICLE INFO

Keywords:
Thermionic energy converter
Graphene
Electrostatic gating
Space charge barrier
Work function

ABSTRACT

Thermionic energy converters (TECs) are a direct heat-to-electricity conversion technology with great potential for high efficiency and scalability. However, space charge barrier in the inter-electrode gap and high anode work function are major obstacles toward realizing high efficiency. Here, we demonstrate for the first time a prototype TEC using a back-gated graphene anode, a barium dispenser cathode, and a controllable inter-electrode gap as small as 17 μm, which simultaneously addresses these two obstacles. This leads to an electronic conversion efficiency of 9.8% at cathode temperature of 1000 °C, the highest reported by far. We first demonstrate that electrostatic gating of graphene by a 20 nm HfO_2 dielectric layer changes the graphene anode work function by 0.63 eV, as observed from the current-voltage characteristics of the TEC. Next, we show that the efficiency increases by a factor of 30.6 by reducing the gap from 1 mm down to 17 μm, after a mono-layer of Ba is deposited on graphene by the dispenser cathode. Finally, we show that electrostatic gating of graphene further reduces the graphene work function from 1.85 to 1.69 eV, leading to an additional 67% enhancement in TEC efficiency. Note that the overall efficiency using the back-gated graphene anode is 6.7 times higher compared with that of a TEC with a tungsten anode and the same inter-electrode gap.

1. Introduction

Electric power can be generated directly from thermal energy by a thermionic energy converter (TEC)[1,2]. During operation, a fraction of the electrons absorb enough heat to overcome the work function of the cathode, leading to thermionic emission [3,4]. The emitted electrons traverse the inter-electrode gap and then are collected at the anode, which has a lower work function. The ideal TEC can operate in a wide range of working temperatures that is at least competitive with most of other thermal-to-electricity technologies [1,5]. Unlike thermoelectrics [6], which have a solid material between the two electrodes, TECs use a vacuum gap between the cathode and anode. This feature radically improves the conversion efficiency by reducing parasitic heat conduction, while also enabling ballistic electron transport.

Since the first reported practical TEC [7], many efforts have been devoted to its development [8–12]. However, TECs have not been successfully commercialized, due to several major challenges [13]. One challenge is the high work function of conventional anode materials, which reduces the output voltage V_{out} and so as the output power P_{out}. The theoretical maximum efficiency for a TEC with a 2 eV work function anode is 3% at cathode temperature of 1500 K, compared to 32% with a 1 eV work function anode [14]. Fortunately, progress has been made recently in the search for ultra-low work function materials [15–17]. Our group has shown that graphene's work function can be reduced to as low as 1 eV by combining electrostatic gating and monolayer alkali metal deposition [18].

Another major challenge is the space charge barrier. This effect manifests when electrons in transit across the inter-electrode gap create a potential barrier that suppresses the emission current, leading to reduced output current I_{out} and thus P_{out}. There are typically three approaches to mitigating the space charge barrier. The first approach is to introduce positive ions, e.g. Cs^+, to neutralize the inter-electrode space charge. Many of the TECs reported in the 1950s – 1980s utilized this approach [7,8]. However, the output voltage V_{out} is typically reduced by 0.3–0.5 eV to maintain this ion plasma, leading to an almost 50% reduction in P_{out}[19,20]. The second approach is to introduce a gate electrode with positive bias between the cathode and anode [21,22]. The additional electrode helps the emitted electrons

* Corresponding authors.
E-mail addresses: hyyuan36@stanford.edu (H. Yuan), rthowe@stanford.edu (R.T. Howe).

http://dx.doi.org/10.1016/j.nanoen.2016.12.027
Received 28 October 2016; Received in revised form 24 November 2016; Accepted 14 December 2016
Available online 15 December 2016

from the cathode to travel across the inter-electrode space to reach the anode. However, very few practical TECs have been reported using this approach, due to a significant reduction of I_{out} from electrons being intercepted by the gate. The third approach is to reduce the inter-electrode gap. It has been calculated that the space charge barrier becomes negligible once the gap is less than several micrometers for practical emission currents [23,24]. Pioneering work using nano-fabrication techniques achieved a 1.7 μm gap size and cathode temperatures as high as 2900 K [11]. However, due to the limited material choices available, the work function for both the anode and cathode was too high to achieve useful conversion efficiencies.

In this study, we demonstrate for the first time a prototype TEC using a back-gated graphene anode, a dispenser cathode [25–27], and a controllable inter-electrode gap as small as 17 μm. We first show that electrostatic gating does change the work function of graphene by observing the current – voltage (I – V) characteristics of the TEC device. By applying a back-gate voltage V_G, graphene's Fermi level can be shifted up due to capacitive charge accumulation, leading to a reduced work function. We then demonstrate that by reducing the inter-electrode gap size, P_{out} increases dramatically due to mitigation of the space charge barrier. Once the gap size is within about 100 μm, a sub-monolayer of Ba will be deposited on the graphene surface from the dispenser cathode at its working temperature, leading to a much lower work function due to the formation of strong dipoles on the surface [28]. Finally, we show that the efficiency of the TEC device can benefit significantly by reducing the graphene work function further through electrostatic gating with this Ba coating.

2. Results and discussion

The structure of the TEC is shown schematically in Fig. 1a. A 20 nm thick layer of HfO_2 is deposited by atomic layer deposition (ALD) on a p^{++} silicon substrate and serves as the gating dielectric (see Supporting Information). A 5 mm^2 piece of graphene grown on copper foil by chemical vapor deposition (CVD) is transferred onto this HfO_2 layer. A back-gate voltage V_G is applied across the HfO_2, controlling the work function of graphene, φ_A, through the electrostatic gating effect [18]. The dispenser cathode is composed of tungsten matrix-impregnated barium compound with a working temperature of 1000 °C in this study. At about 600 °C, Ba starts to disperse and diffuse to the cathode's surface, reducing the cathode work function φ_C. At the working temperature, Ba is emitted from the cathode surface. If the graphene anode is close enough to the cathode surface (< 100 μm), a monolayer of Ba will gradually form on the anode within a couple of hours, which is essential to lowering the anode work function. The dispenser cathode is mounted on a 5 axis manipulator [29], which has 0.7 μrad angular and 30 nm translational precision. This manipulator controls the cathode position and is used to reduce the inter-electrode gap size. The TEC prototype is tested in an ultra-high vacuum (UHV) system, with a base pressure of 1×10^{-10} Torr. At the working temperature, the pressure is below 2×10^{-9} Torr.

The I – V characteristics for an ideal vacuum TEC device with negligible back emission current from anode to cathode are shown in Fig. 2a. The saturation current is given by the Richardson-Dushman equation,

$$I_S = AST_C^2 e^{-\frac{\varphi_C}{kT}} \quad (1)$$

where A is the Richardson-Dushman constant estimated to be 70 A/cm^2K^2 for the dispenser cathode in use here, S is the surface area of the electrodes, and T_C is the cathode temperature. When an external bias V_{out} is applied with $V_{out} < (\varphi_C - \varphi_A)/e$, all thermionically emitted electrons have enough energy to travel through the inter-electrode gap. As a result, I_{out} remains constant as I_S, also known as the saturation region. On the other hand, when $V_{out} \geq (\varphi_C - \varphi_A)/e$, only a fraction of emitted electrons can reach the anode due to the applied electrical potential barrier.

$$I_{out} = AST_C^2 e^{-\frac{\varphi_A + eV_{out}}{kT_C}} \quad (2)$$

This is called the Boltzmann region. Note that the Boltzmann region appears to be a straight line in the I – V characteristics under log scale, whose slope is only depended on the cathode temperature T_C. With T_C fixed, the anode work function φ_A determines the intercept of the Boltzmann line, which is the feature we use to determine if there is any change of φ_A. We can also estimate φ_C by fitting the saturation current I_S. Compared with the ideal I – V characteristics, I_{out} will be significantly lower for real TECs due to the space charge barrier (Figure 2.1 a).

We start our demonstration by measuring the electrostatic gating graphene effect on the TEC performance. We first run the dispenser cathode for a couple of hours to stabilize the system by monitoring the saturation current I_S. The cathode is set to operate at a relatively low temperature, around 750 °C, such that I_S is small enough to not cause significant space charge barrier even with a large inter-electrode gap size of approximately 1 mm. This also ensures a clean graphene surface without any deposited Ba from the dispenser cathode. The I — V characteristics are shown in Fig. 2c with the back-gate voltage V_G ranging from −6 to 8 V. The shift of the Boltzmann line, 0.63 eV, corresponds to change of the graphene anode work function due to electrostatic gating, which is characterized by

$$\varphi_A = sign(E_G - E_D)\hbar v_F \sqrt{\pi \varepsilon_{ox} |E_G - E_D|/e} + \varphi_{A0} \quad (3)$$

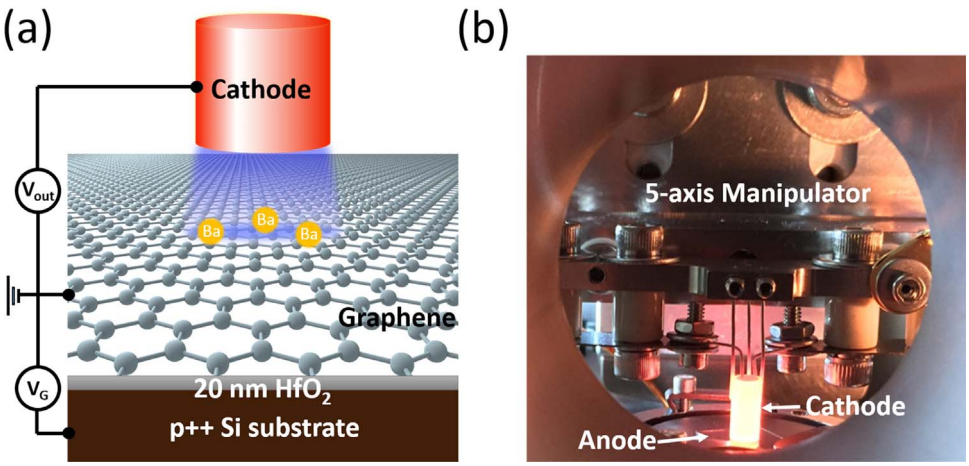

Fig. 1. (a) Schematic sketch of the TEC prototype. The contact to graphene is via a 50 nm thick Pd pad deposited by thermal evaporation. Details of the back-gated graphene anode are discussed in more detail in reference 18. (b) Photograph of the TEC prototype during operation [14]. Note: the anode shown here is not the graphene anode.