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Efficient utilization of multilayer graphene towards thermionic convertors

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ABSTRACT

In this paper a comprehensive model to investigate the thermionic emission from few layer graphene (FLG) structures operating at finite temperature (T) and its feasibility towards thermionic energy conversion scheme as cathode, has been proposed. Taking into account the stacking dependent energy dispersion for the evaluation of density of states of Fermionic electrons and Fowler's treatment of the electron emission, the analytical expressions for the thermionic flux from ABA/ABC stacked FLG surfaces have been derived and shown to be an increasing function of number of constituent layers (N). In contrast to the usual RD law ($\propto T^2$) thermionic flux-temperature scaling, ABA and ABC stacked FLG have been identified to display $\propto T^3$ and $\propto T^{1+2/N}$ temperature scaling. Utilizing the competence of FLGs to deliver substantial thermionic flux in fabricating the FLG based cathodes, an appropriate operating regime for the constituent parameters of the thermionic convertors (TCs) describing efficient energy conversion, has been specified. As a remarkable feature, FLG based cathodes provide flexibility to operate TC at low cathode (and high anode) temperature, with a sustained optimum efficacy (equal to the monolayer graphene). As an illustrative case, a TC configured with FLG based cathode ($N = 10$, ABA stacking, ~900 K) and low work function (Cesium coated) metallic anode (2.0 V, 400 K) has been identified to display ~55% of the conversion efficiency (equivalent to ~82% of the Carnot efficiency). On the basis of analytical formulation, appropriately tuned FLG based cathode operating at low temperature, is proposed as a promising contrivance in achieving efficient energy conversion of heat into electrical power.

1. Introduction

Graphene based nano-structures have conceived significant attention in past few years on account of its fascinating electronic and mechanical properties [1–3], and its utility towards nano scale electronics [4–7] and sensor technologies [8]. Specifically, intriguing properties of the few layer (multilayer) graphene (FLG) are exploited for numerous novel schemes for local doping [9], surface functionalization [10], thin nano-electronic circuits [11] and photovoltaic devices [12]. Practical methods such as mechanical cleavage [4], atmospheric pressure graphitization of SiC [13], chemical oxidation of graphite [14] and chemical vapor deposition (CVD) [15] etc., have been developed to produce monolayer/multilayer graphene (FLG/SLG) in laboratory and at commercial level. In a recent investigation, the development of FLG structure of pre-defined thickness (number of layers N) has been reported by Krajewska et al. [16]; in this method the deposition over substrate is followed by a subsequent transfer process of deposited stack to any arbitrary substrate. Such nano-structures operate efficiently at high temperature (~1800 K) without changing its inherent statistical features [17–21]. The FLG configured with ABA and ABC stacking is found to be thermodynamically stable structures [22]; such stacking can be prominently visualized in the structures of trilayer graphene (see Fig. 1 of Reference [23]). In fact, the FLG has been seen to retain the characteristic properties like high stiffness, ultrahigh electrical conductivity and extreme mobility etc. [24], of the monolayer graphene (SLG); however the respective strengths depends on the energy band structures [25–27].

The electrical properties of the monolayer graphene are primarily driven by the availability of free electrons in linear band

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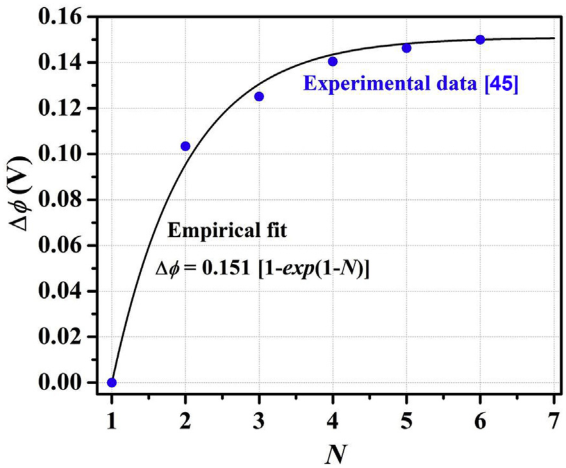

Fig. 1. $\Delta\phi$ as a function of number of layers (N) in FLG structure: Empirical fit of the experimental data (Ref. [45]).

structure (linear energy dispersion) in the proximity of the Fermi level [24]. In case of FLG the electronic properties become sensitive to the stacking order and the sheet thickness (number of constituent layers N) [24–27]. For example, bilayer graphene (BLG) mimics a tunable band gap semiconductor [28] while in trilayer graphene (TLG) the electronic structure is described via complex manifestation of massless SLG and massive BLG sub-bands [29]. The literature [30] reveals that the electronic band structure in the FLG is characterized by non-parabolic energy dispersion, in contrast of linear dispersion of SLG and parabolic dispersion of bulk graphite. In an elegant work, taking the non-parabolic dispersion for the ABA/ABC stacking FLG into account, the current (flux) temperature scaling for the thermionic emission from FLG has been investigated by Ang and Ang [30]. However their analysis is constrained to the Maxwellian distribution of electrons in FLG and applicable to the high temperature regime only. The innovative concept of photon enhanced thermionic emission [31–33] has revived the research horizon of the thermionic emission based phenomena/devices; in particular towards 2D materials whose electronic properties are sensitive to the operating temperature and may efficiently be tuned. Concerning high planar density associated with 2D monolayer graphene and its sustenance to operate in high temperature regime, Liang and Ang [34] identified SLG to exhibit current temperature scaling different from that of the conventional Richardson law and proposed a promising utility of SLG based cathode in thermionic convertors (TCs). Their investigation is further taken up by Misra et al. [35] where the analysis for the electron emission from monolayer graphene has been modified by including Fermionic nature of the electron energy distribution alongwith temperature dependence of the intrinsic Fermi level. Based on their analysis a SLG (monolayer graphene) based TC operating at moderate temperature (~1200 K) with metallic anode, is proposed to achieve ~56% of the conversion efficiency. Importantly, the effect of graphene based structures on TCs has experimentally been also verified where a prototype TC configured with back gated graphene anode is shown to significantly improve the conversion efficiency [36]. In a recent work [37], solid state thermionic devices configured with the graphene electrodes sandwiching Van der waals heterostructures has been proposed and its intriguing thermionic emission properties are exploited; in this analysis Liang et al. [37] have predicted to harvest the waste heat at low temperature (400 K) by an efficiency of ~7%, using WSe_2 or $MoSe_2$ as thermal insulation. Such efficient TCs could be utilized as an alternative energy source in power plants, industries and numerous space applications [38–44].

Concerning the significance of non-parabolic energy dispersion of electrons over electronic properties [30] and thermodynamically stable configurations (ABA/ABC) [21] of FLG structures, it is worth to critically examine the characteristic features of electron emission from the FLG structures and then to prolong the notion to FLG based cathodes in the thermionic conversion scheme. With this motivation, we analyze the thermionic emission from the multilayered graphene (FLG) structures configured with ABA/ABC stacking. The objective of this analysis is twofold. First we formulate the process of thermionic emission from the ABA/ABC stacked FLGs. The formulation include the non-parabolic energy dispersion for FLG in order to evaluate the adequate density of states in the electron population, Fermi Dirac (FD) distribution of the electron energy and Fowler's treatment of the electron emission. In addition, the work function dependence on the number of constituent layers (N) in FLG structure [45] and linear temperature dependence of the intrinsic tuned Fermi level [46] has also been taken care of in the analysis. Next, on the basis of analytical treatment, the expressions for the thermionic flux corresponding to ABA/ABC stacked FLG have been derived and its dependence on numerous FLG parameters has also been analyzed. Furthermore, we examine the feasibility of the FLG structures in configuring an efficient TC. The tunability of the graphene based FLG parameters (like work function/Fermi level) to desired extent via various technological means [47–51] and its flexibility to operate at higher temperature, intends an option to utilize it as FLG based cathodes in the energy conversion scheme. For the illustration of the conceptual basis, a TC setup is simulated via combining FLG based cathode (emitter) and metallic anode (collector) with an external load. In the TC setup, FLG based cathode is kept at higher temperature and negative bias with respect to the collector plate which is maintained at lower temperature; the excessive flux transported through the anode, may be extracted across the load as electrical power. Using the FLG based TC setup, the conversion efficiency has been depicted as a function of constituent parameters; based on the calculations for conversion efficiency a parameter regime describing efficient TC operation has been identified.

The paper is organized as follows: Section 2 is devoted to the analysis for the thermionic emission of electrons from multilayered graphene (FLG) structures; the numerical results for the thermionic flux, based on the analytical formulation have been analyzed and discussed in Section 3. The applicability of the electronic properties of the FLG based structures in thermionic energy conversion scheme has been established in Section 4 while the respective analytical results and physics interpretation has been given in Section 5. A summary of the outcome from this analysis in Section 6 concludes the paper.

2. Evaluation of the thermionic flux from multilayer graphene

The electronic properties driven by electron emission process of any material in principle, depends on the available free electron population and its statistical distribution in the lattice [52]. In this course, the emission flux significantly depends on the stacking order for few layer graphene (FLG) structures [24–27] as a particular stacking specifies unique energy dispersion describing electron population in FLG. Two specific configurations of FLG structure viz. ABA and ABC stacking are observed to operate in stable thermodynamic mode [22]. Herein this analysis, we evaluate the thermionic emission flux for the two aforementioned specific stacking, operating at finite temperature. For the evaluation purpose we take account of Wallace [53] assumption for the charge