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Graphene-metal-semiconductor composite structure for multimodal energy conversion☆,☆☆

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ABSTRACT

In this paper we present a new approach to enhance the energy conversion efficiency of metal-semiconductor junction by integrating CVD-grown graphene on top of Pt/Si junction. Flexoelectric behavior can be observed and further modulated in the fabricated composite structure as a result of the mismatch in the mechanical and thermal properties and the residual stresses at the interface of the structural layers induced from the thin-film deposition processes. Moreover, graphene layer acts as an antireflection coating to the metal-semiconductor structure, therefore, upon exposure to a heat flux or infrared radiation, the thermionic behavior can also be observed by forming a carrier-free layer as a result of charge transfer from graphene to metal. Therefore, we suggest that due to the heterogeneous composite nature of the proposed structure, both thermionic and flexoelectric energy conversion behaviors can work in conjunction upon exposure to heat flux or IR radiation increasing the overall efficiency of the device. The polarization induced by varying the radius of curvature from 600 to 2000 mm by applying bending stresses was investigated experimentally. Meanwhile, due to the cluster-growth nature of the ALD-platinum catalyst layer, a strong correlation was observed between the resulting graphene layer thickness and the Pt catalyst layer thickness, which subsequently had a strong impact on the induced polarization. A polarization current of up to 7.4 mA was detected when the composite structure was bent through a 600-mm radius of curvature. Residual stresses at the interface of the different layers were estimated experimentally in the order of 85–217 MPa. The effect of thermally induced stresses, residual stresses at the interface layers, thickness of graphene layer, and radius of curvature were investigated theoretically using multi-scale FEM and first-principle calculations using tight binding method. Theoretically, it was confirmed that non-uniform strain results in non-uniform appreciable graphene band gap opening (in the order of 0.6–1.02 eV), in addition to non-uniform change of the band structure across the width and thickness. Both effects eventually resulted in net polarization. FEM confirmed that thermo-mechanically induced strains could further enhance the power output of the device by inducing a flexoelectric current combined with the thermionic response. This is verified by estimating a graphene lattice distortion in the order of 0.31 Å in response to 2-mW heat flux, which corresponds to approximately 12.6% distortion in the graphene lattice parameter. Controlling the film residual stresses at interface between the layers can further modulate the mismatch and maximum lattice distortion.

1. Introduction

Graphene is emerging as ideal candidates for thin-film devices and combination with other materials to form composite structures, which can provide unprecedented solutions to various applications including, energy [1–4], electromechanical [5,6], sensors [7,8], crashworthiness [9], and semiconductor [10,11] applications.

Most energy conversion techniques nowadays are based on semiconductors devices. Solar energy, hydrogen production and water splitting are the recent research topics involving the fabrication of different structures of semiconductors to enhance the photoelectric effect. The incident photons energy is related to the band gap of the materials to excite electrons from the orbitals. The recent fabricated electrodes used are semiconductors such as Si, CdS, GaAs, ZnO, Ta_2O_5, and TiO_2 [12]. Metal-semiconductor

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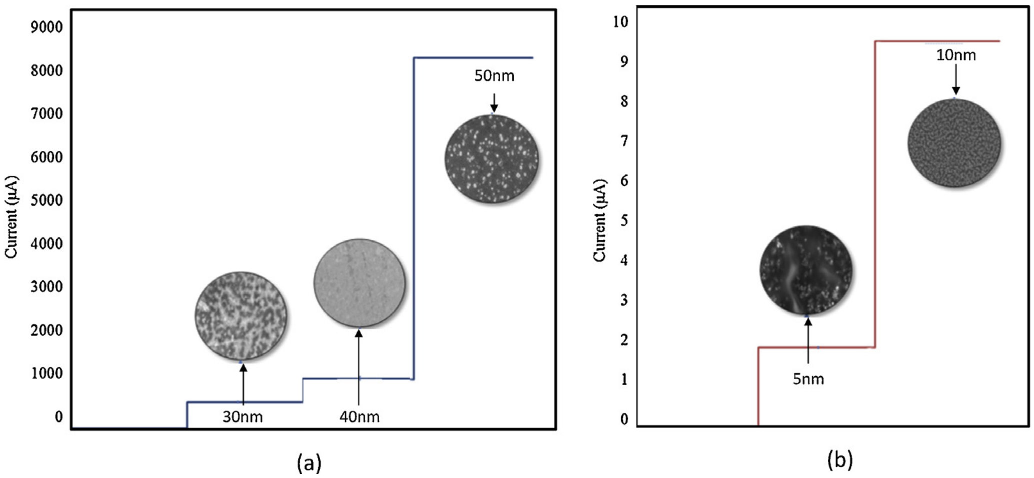

Fig. 1. Schematic diagram of the working principle of the graphene-metal-semiconductor composite structure showing SEM images of the top view of the graphene and platinum thin films.

junctions, e.g., Schottky diodes has also been utilized in energy conversion as in developing highly efficient solar cells and electrochromic devices [13,14], hydrogen detection in oxygen atmosphere [15], and detection of excited electrons from the chemisorption of oxygen and hydrogen atoms and the transfer of electrons through the Schottky barrier [16]. Accordingly, the main idea of this research is to enhanced the energy conversion efficiency of metal-semiconductor junctions by employing different modes of energy conversion simultaneously, e.g., piezoelectric and thermionic. One important mode of which is flexoelectricity.

Flexoelectricity is an electromechanical response as a result of a relation between strain gradient and the dielectric polarization. Centrosymmetric materials have symmetric order of atoms within the lattice. However, a non-uniform strain gradient across the material's thickness/surface can break the centrosymmetry leading to an induced polarization vector inside the material. Flexoelectric effect is represented in a four-ranked tensor μ_{klij}.

The flexoelectric effect can therefore be described by the following constitutive relationship [17]:

$$P_i = X_{ij}E_j + e_{ijk}u_{jk} + \mu_{klij}\frac{\partial u_{kl}}{\partial x_j} \tag{1}$$

where P_i is the electric polarization, E_j is the macroscopic electric field, u_{jk} is strain tensor, $\frac{\partial u_{kl}}{\partial x_j}$ is the spatial gradient, X_{ij} clamped dielectric susceptibility and finally e_{ijk} is the piezoelectric tensor.

The flexoelectric behavior of graphene has been fundamentally explained in literature by the means of mathematical model to the response of graphene sheets under mechanical deformations by using Density Function Theory (DFT) [18]. The calculations showed that there is linearity in the flexoelectric effect and the curvature of carbon atoms in the sheet with various atomic orders. In addition, more studies have been performed on the ability of changing the piezoelectric property of graphene by creating holes in the Graphene structure to break the centrosymmetery [19]. Moreover, doping Graphene with different atoms like hydrogen or flourine were studied to enhance the piezoelectric property [20].

Therefore, in this paper we attempt to build a new application in order to enhance the energy conversion efficiency of metal-semiconductor junction by integrating a CVD-grown graphene layer on top of Pt/Si junction to form a composite structure (Fig. 1). As a result of the mismatch in the mechanical and thermal properties between the various components of the composite structure in addition to the residual stresses at the interface of the structural layers induced from the thin-film deposition processes, non-uniform strain gradient is induced in the graphene layer leading to an observable flexoelectric behavior which can further be modulated by increasing the strain non-uniformity, e.g., by increasing the induced residual stressed between the layers. For example, upon heating the top surface of the graphene layer stress/strain gradient forms across the thickness of the graphene layers leading to polarization and therefore energy conversion by the flexoelectric mode. Moreover, graphene layer acts has antireflection coating to the metal-semiconductor structure [21], therefore, upon exposure to infrared radiation, the thermionic behavior can also be observed by forming a carrier-free layer as a result of charge transfer from graphene to metal until their Fermi levels align and graphene becomes p-doped as its Fermi level shifts (Fig. 2(a)). At the metal-semiconductor junction, a depletion region is formed as carriers migrate from semiconductor to metal. Therefore, we suggest that due to the heterogeneous composite nature of the proposed structure, both thermionic and flexoelectric energy conversion behaviors can work in conjunction upon heat flux or IR radiation exposure increasing the overall efficiency of the device upon exposure to sufficient power.

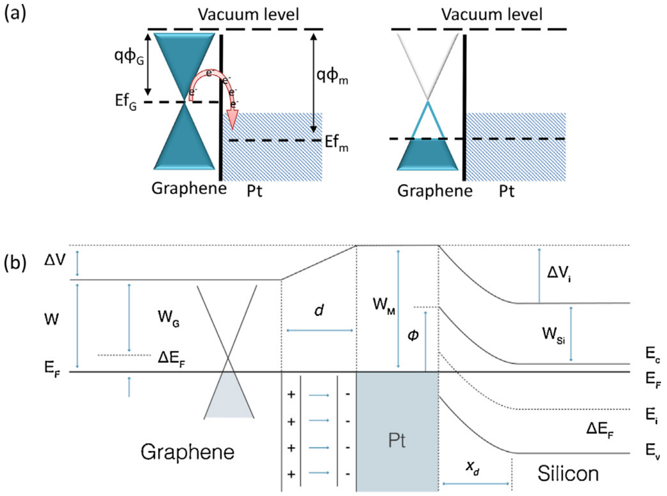

Fig. 2. (a) P-doping of graphene due to difference in work functions, (b) the energy-band showing the two junctions where a Schottky barrier is formed.

Accordingly, in this paper, experimental and theoretical (i.e., multi-scale FEM, and first-principle calculations using tight binding method) investigations of the mechanical and thermo-mechanical behavior of the proposed graphene-metal-semiconductor compos-