Graphene-Based Nanostructures for Advanced Sensing Applications

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ABSTRACT

Nanostructured Schottky junctions based on graphene/platinum grown on different silicon substrates are fabricated and investigated for sensing applications. Carrier transport mechanisms are interpreted on the basis of studying the band diagrams and theoretical models, both of which verified tunneling as the dominant charge transport in the device. Investigations verified that sensing behavior is dominated by the carrier distribution function at the metal-semiconductor junction, which further implies that substrate's resistivity, fabrication temperature and doping level have an insignificant effect on the sensing behaviors. Application of the device for infrared sensing is demonstrated.

Keywords: Graphene, Schottky, sensor, infrared, nanostructure

1 INTRODUCTION

In past decades, scaling down of solid-state sensors resulted in improved device efficiency and capacity. However, the ability to scale down devices comes with challenges in designing and developing nanostructures that operate properly in increasingly smaller environments. Schottky diodes can replace conventional PN junctions and bipolar transistors in scaled down solid-state sensors, offering faster response and lower threshold voltages [1]. Schottky diode-based sensors generally consist of a metal-semiconductor (M-S) junction. The most common choices of metals are catalytic-type noble metals (e.g., Au, Pt, and Pd) [2,3]. Schottky diodes have been implemented in developing highly efficient sensors, solar cells and electrochromic devices [4-6]. Graphene ultrathin sheets are emerging as ideal candidates for thin-film devices and combination with other semiconductor materials such as silicon. They have been produced in the form of ultrathin sheets consisting of one or a few atomic layers directly grown by chemical vapor deposition (CVD) [7,8] or by solution processing [9,10] and then transferred to various substrates.

In this work, we have implemented a direct, simple, reusable, isotropic, wide-range, and ultrahigh sensitive range of physical and chemical sensors based on graphene-Schottky junctions. The sensor is based on a nanostructured array of graphene grown on a platinum/n-Si substrate. The new sensor structure (Fig. 1) is a Schottky barrier diode, based on formation of a M-S junction of n-type silicon substrate and ultrathin film platinum integrated with a graphene layer [11-13].

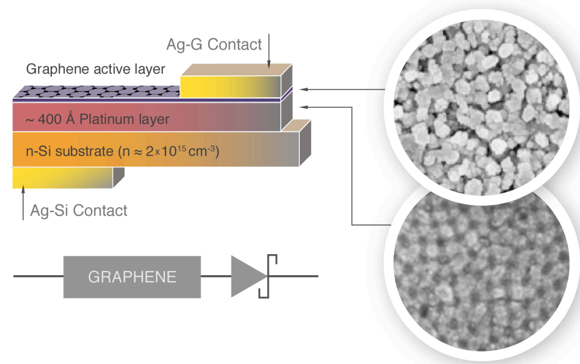

Figure 1: Schematic of the device showing SEM of the graphene and platinum microstructures [13].

Sensing behavior of the proposed device is investigated in this paper. Enhanced performance of both sensors is demonstrated mainly due to the band interaction at the graphene-platinum-silicon junctions, which yields stronger forward/reverse currents in response to stimulus.

2 STRUCTURE AND FABRICATION

2.1 Fabrication

Graphene high-uniformity film with small flakes embedded with platinum particles was synthesized using two deposition steps. The first deposition step of the platinum catalysis was performed in Atomic Layer Deposition (ALD) using the Cambridge NanoTech Savannah ALD deposition system. The precursor used was Trimethyl(methylcyclopentadienyl)platinum(IV), with high purity O_2 used as an oxidizing agent. Deposition temperature is 275°C for 50 – 300 cycles to produce the catalysis Pt thin film in approximate thickness of 40 to 300 Å. The second deposition step was utilized Plasma Enhance Chemical Vapor deposition (PECVD) using Oxford Instruments, PlasmaLab 100 PECVD System at 600°C in a methane (CH_4) rich environment [13].

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3 GRAPHENE−SCHOTTKY DEVICE SENSING PRINCIPLE

3.1 Carrier Transport Mechanism

To study the flow of carriers in the proposed Gr/Pt/n-Si heterojunction, we divide the structure into two consecutive junctions (Fig. 2): (a) Graphene-Metal junction formed at the Gr/Pt interface, in which a carrier-free layer formed as a result of charge transfer from Gr to Pt until their Fermi levels align [14, 15], and (b) conventional Metal-Semiconductor junction formed at the Pt/n-Si interface, where the formation of a depletion region is due to the immigration of carriers from Si to Pt [16].

At the Gr/Pt junction, a dipole is formed with a potential barrier (ΔV), and graphene becomes p-doped due to the shift of its Fermi level. When a forward or a reverse voltage is applied across this junction, current flows in both directions and the I-V characteristics of such a junction is almost symmetric, as electrons tunnel through the potential barrier in both directions [14, 15]. Whereas at the Pt/n-Si junction a Schottky barrier (Φ) is formed, the I-V characteristics of the second junction depend on the carrier distribution function and concentration at the silicon surface. For low doping concentration, electrons can flow from Si to Pt when positive voltage is applied at the Pt electrode, while they cannot overcome the barrier if the positive voltage is applied at the Si electrode.

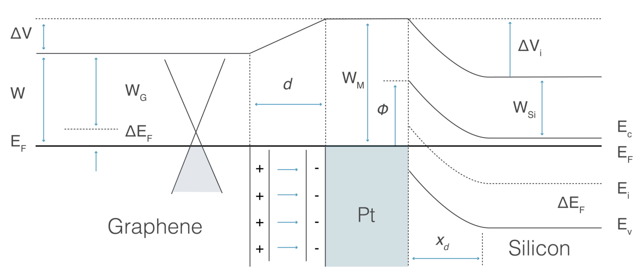


Figure 2: Energy Band Diagram of the proposed structure, showing two junctions.

Consequently, the device has rectifying characteristics as shown in Fig. 3-a. According to the thermionic emission and diffusion theories of Schottky diodes, the dependence of forward current on the applied voltage is given by the expression [16]:

$$I = AA^{**}T^2 \exp\left(-\frac{q\Phi}{kT}\right)\left\{\exp\left(\frac{qV}{\eta kT}\right)-1\right\} \qquad (1)$$

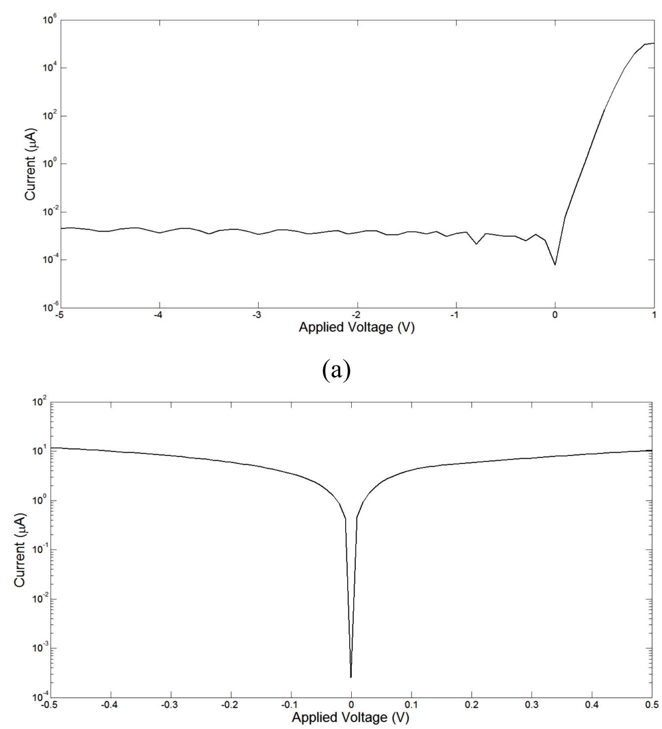
where A is the junction's surface area, A^{**} is the Richardson constant, Φ is the zero bias Schottky barrier height in eV, q is the charge of one electron, V the applied voltage, T the absolute temperature in Kelvin, k is the Bolstmann's contstant, and η is the ideality factor. For high carrier concentration at the Si surface, the width of the depletion region decreases and the height of the barrier is lowered [16, 17], consequently, electrons can tunnel through the potential barrier in both directions according to the applied voltage and the I-V curve becomes nearly symmetric as in Fig. 3-b. The tunneling current can be calculated from the product of the carrier charge, velocity, density, and probability of tunneling, which can be modeled by [16]:

$$I = A\,q\,v_R\,n\exp\left(-\frac{4}{3}\frac{\sqrt{2qm^*}\,w\Phi^{1/2}}{\hbar}\right), \qquad (2)$$

where A is the junction's surface area, q is the charge of one electron, v_R is Richardson velocity and is given by:

$$v_R = \sqrt{\frac{kT}{2\pi m}}, \qquad (3)$$

where T is the absolute temperature in Kelvin, k is the Bolstmann's constant, m is the mass of electron, n is the density of carriers in the semiconductor, m^* is the effective mass of electrons in silicon, w is the barrier width, Φ is the barrier height in eV.



(a)

(b)

Figure 3: measured I-V curves of (a) rectifying Gr/Pt/n-Si heterojunction (b) tunneling Gr/Pt/n-Si heterojunction.

3.2 Sensing Mechanism

The working principle of the proposed sensing nanostructure is based on the interaction of the physical signal that is being sensed with the graphene film. Moreover, when this signal penetrates through the graphene film and reaches the Pt/n-Si junction, more free electrons are generated and the concentration of carriers at the silicon side increases, which shifts the Fermi level up, causing the Schottky barrier height (SBH) at the Pt/n-Si junction to decrease. If the device is biased at a constant voltage, the variation in SBH results in a detectable current change in both of the rectifying and tunneling junctions.

The physical properties of graphene are highly dependent on the position of its Fermi level. Therefore, the applied bias voltage on the structure is an issue of high importance. Consider an example of an IR photodetector, which will be discussed in detail in Section 4. As discussed in [18-20], the optical absorption of graphene is proportional to its doping. Since graphene is doped according to the applied voltage, its absorption will vary and different sensitivities are expected for different bias voltages. In applications that require certain optical properties of graphene where a high voltage should be applied at the Gr/Pt junction, the use of rectifying Schottky Pt/n-Si junctions becomes necessary to avoid high leakage of current.

It was noted through various experiments that the dominance of the tunneling versus thermionic currents can be attributed to the Pt/n-Si interface lattice defects, which result in variable carrier concentrations at the interface, as previously explained in Section 3.1. Accordingly, it is concluded that the substrate's resistivity, fabrication temperature and doping level have insignificant effect on the I-V characteristics and sensing behaviors of the device.

4 GRAPHENE BASED IR SENSOR

The Gr/Pt/n-Si structure can be used as an infrared (IR) detector. As illustrated in Fig. 4, when light is incident on the structure and as IR power reaches the Pt/n-Si junction, a detectable change in current is observed due to the change of the barrier height. The graphene film, if fabricated at a matching thickness, enhances the absorption of the incident light as it decreases the reflected power. One might explain this as the graphene film acting as an antireflection coating for the Pt/n-Si junction. Based on the desired wavelength, the reflection properties of the device can be changed by changing the number of layers of graphene, and impedance matching can be achieved with suitable layers [21].

Furthermore, chemical and electrical doping has proven a good solution to drive the Fermi level down, which greatly optimizes the impedance matching properties of the graphene layer [18, 21]. Moreover, the broad optical absorption in graphene can be controlled through electrical gating: by shifting the electronic Fermi level, one can controllably change graphene's optical transitions. The I-V curve is shown in Fig. 5 when the device is exposed to IR light of peak wavelength of 912 nm. It is clear that the sensitivity decreases at the application of a reverse bias voltage. This is due to the variation of optical properties of graphene with applied voltage.

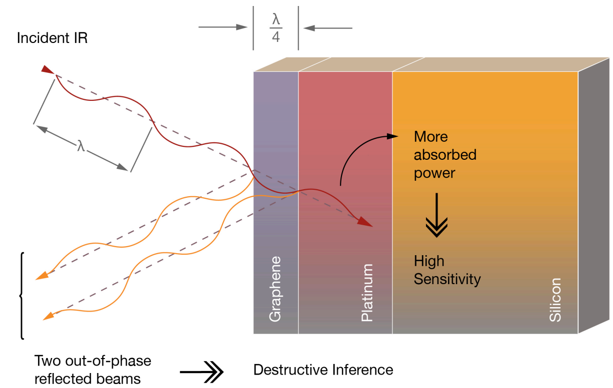


Figure 4: Principle of operation of Gr/Pt/Si IR detector.

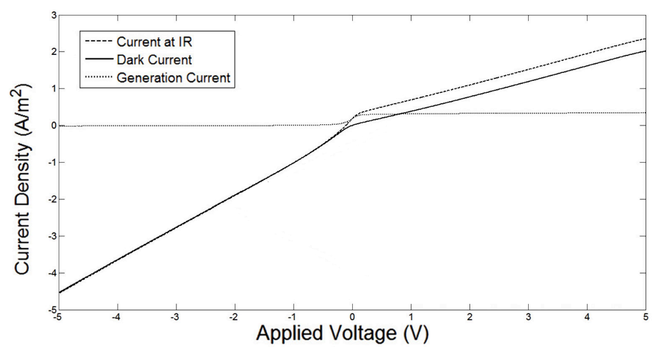


Figure 5: Effect of IR on I-V curve of the Gr/Pt/Si structure.

5 CONCLUSION

In this paper, we have described and demonstrated a new device concept by integrating graphene to a Schottky junction. The key idea is that the current flowing through the Schottky junction is dominantly controlled by the junction's characteristics (i.e., SBH, and barrier's width), which are highly sensitive to the stimuli around the junction, such as IR in our case. It was further demonstrated that our proposed device's SBH could be effectively modulated according to tunneling or thermionic modes by controlling the carrier concentration at the metal-semiconductor junction, which further demonstrates that this sensing principle can be effective in sensing other sorts of radiation or other biochemical species. To enhance the device performance, a three terminal contact would enable the control of both junctions separately, for example: if the Gr/Pt junction performs better when forward biased and a reverse biased Pt/Si junction is needed, it can be achieved.

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