Effect of ethanol concentrations on few layer Schottky graphene transistors

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Abstract. We have studied the effect of positive and negative back gate voltage on the Schottky barrier of few layer graphene transistors (devices) in the presence of Air, Nitrogen and different ethanol vapor concentrations. The presence of the Schottky barrier in these devices is attributed to unintentional doping of the different areas of the graphene flake and is modulated by applying a positive gate voltage, increasing the source-drain current.

1. Introduction
Interest in nanomaterials has been growing rapidly for the past several years. Particularly graphene, which is a monolayer of carbon atoms arranged in a two dimensional honeycomb structure and is the starting point for any material derived from carbon (fullerenes, nanotubes or graphite). Graphene-based rectifying devices have been investigated only scarcely due the complex processes required to achieve both p- and n-doped semiconducting graphene. Graphene-based pn junctions can be achieved by chemically doping different areas of the same graphene flake, or by appropriate electrical gating [1, 2]. However, such junctions would not be suitable for logic applications, as graphene would still retain its semimetallic character. A way around this problem would be to use graphene in conjunction with a semiconductor, in order to establish a metal-semiconductor Schottky junction [3]. Alternatively, one could reverse the role of the graphene and the semiconductor in the metal-semiconductor junction, for example, by rendering graphene semiconductor and using a traditional metal as electrode. The latter approach has been achieved and modeled by, e.g., considering semiconducting graphene nanoribbons in contact with metals [4]. A Schottky junction can also be formed by bringing semiconducting graphene oxide, obtained by either wet chemistry methods [5] or plasma oxidation [6, 7], in contact with a suitable metal or even with pristine graphene itself. In a Schottky diode the forward current is due to

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majority carriers flowing from the semiconductor to the metal; on the other hand, in a traditional semiconducting $pn$ diode, minority carriers are responsible for electrical conduction.

In this work we report the effect of applying positive and negative back gate voltage on the Schottky barrier of few layer graphene (FLG) transistors in the presence of Air, $N_2$ and different ethanol vapour concentrations (EVCs).

**2. Samples and experimental details**

To fabricate the FLG devices, heavily n-doped (100) wafers with dopant concentration of $N_A = 10^{15}$ cm$^3$ and resistivity $0.002 – 0.005 \ \Omega \cdot cm$ were used as substrates as well as the back gate electrode with a thermally grown oxide layer of thickness of 280 nm, which acts as the dielectric, Ti/Au contacts were evaporated after optical (wider contacts) and electronic lithography (thinner contacts), and structured by the lift-off technique. After the device was fabricated, it was placed in a small chamber connected by a tube to a container of vapor mixture. Concentration of organic vapors was controlled by mixing $N_2$ gas and measured by gas detector. All electrical measurements were carried out by using a DC supply at atmospheric pressure.

Fig. 1(a) shows the optical image of the graphene sample (indicated by the arrows) and contacted by source (S) and drain (D) electrodes, Raman measurements were performed in three different regions of the sample, which are indicated by the numerated arrows. From the Raman spectra (Fig. 1(b)) we can see three different regions: region 1 (solid line) is a monolayer; region 2 (dashed line and middle arrow) ~ three layers and region 3 (dotted line) a bilayer graphene. The numbers in arrows are in correspondence with the numbers in the Raman spectra. On the other hand, it is well known that graphite has three intense Raman features at $\sim 1580$ cm$^{-1}$ (G band), $\sim 1350$ cm$^{-1}$ (D band) and $\sim 2700$ cm$^{-1}$ (2D band) [8]. The G band is due to double degenerate $E_{2g}$ mode at the Brillouin Zone center, whereas D band arises from defect mediated zone-edge (near K point) phonons, this band is present in our sample because of the small sample width which is less than 600 nm. The 2D band originates from second order double resonant Raman scattering from zone boundary, $K + \Delta K$ phonons.

![Figure 1](image)

**Figure 1.** a) Optical image of graphene sample with three different regions, indicated by the arrows; b) Raman spectra of the three different regions of the sample, showing the presence of a monolayer (number 1), bilayer (number 3) and three layer graphene (middle arrow and curve). The inset shows a shift of the G band in the three different regions.
3. Results and discussions

Figure 2 shows the output characteristic of the studied sample, after an annealing treatment in Hydrogen (H<sub>2</sub>)/Argon (Ar) atmosphere at 200 °C for 1 hour, in the presence of dry air and applying three different positive gate voltage. From this figure we can see the reduction of the Schottky barrier as the positive gate voltage increase. The same behaviour was observed in all the samples that were measured after annealing process. On the other hand, it is well know that the cleaning process is effective and yields significantly improved structural and electronic properties of graphene [9] without applying gate voltage, in the same way, previous studies involving dielectrophoresis (DEP) assembled reduced graphene oxide (RGO) with Au electrode have shown that mild annealing reduces the sample resistance and improves the on-current of the field effect transistors [10].

![Figure 2](source-drain_current.png)

**Figure 2.** Source–drain current as a function of the source-drain voltage for 0.0 V, 5.0 V and 20.0 V at the presence of dry air.

With the aim of stabilizing the source - drain current, the measured were done during several cycles, in the presence of dry Air by applying different back gate voltages. After this, the measurements were done in the presence of N<sub>2</sub> and different ethanol vapor concentrations. The results are shown in Fig. 3. In this figure, the source – drain current (I<sub>d</sub>) as a function of source – drain voltage (V<sub>d</sub>) is also swept from - 2.0 V to 2.0 V, for zero (a) and negative (b) back gate voltage (V<sub>g</sub>). Comparing Fig. 2 and Fig. 3, we observe that: the I<sub>d</sub> current is almost zero ~ between -0.5 V and 0.5 V, the current decreased from µA (dry Air) to nA range and remains almost the same for zero and negative gate voltage at the presence of N<sub>2</sub>, 750 ppm and 3800 ppm EVCs. The same way, we note that I<sub>d</sub> current, in N<sub>2</sub> and different EVCs, is almost symmetrical for forward and reverse bias, which suggests two identical Schottky barriers (SBs) established between the FLG and the Ti electrodes. The Ti-FLG-Ti device can therefore be modeled by considering two Schottky diodes connected back to back as reported in the literature [11]. This kind of behavior was also observed in single layer graphene (SLG) samples, previously exposed to oxygen plasma treatment [11], which were named semiconducting single layer graphene (SSLG). The authors argued that after the plasma treatment a Schottky barrier (SB) arises from the difference between the work function of Chromium metal (ϕ<sub>Cr</sub>= 4.5 eV) and SSLG (ϕ<sub>SSLG</sub> ~ 5.0 eV). The later work function increased from 4.3 eV to 5.0 eV after the O<sub>2</sub> plasma treatment due to the covalent interaction between the SLG basal plane and oxygen atoms, introducing surface dipole moments. Schottky behavior was also reported in RGO samples contacted with Ti/Au electrodes [12]. However, our samples show this effect without any chemical treatment.
Figure 3. \(I_D\) current as a function of \(V_D\) for zero and negative gate voltage in the presence of different ethanol vapor concentrations.

The Schottky behavior of our samples could be explained in terms of unintentionally doping, which probably occurred after lithography process or during the evaporation process of thicker metal electrodes (S and D in Fig. 1). This doping probably increased the work function of FLG from \(\sim 4.3\) eV to \(\sim 5.0\) eV as manifested by the different peak positions of the G band (1590 cm\(^{-1}\) for region 1, 1584 cm\(^{-1}\) for region 2 and 1583 cm\(^{-1}\) for region 3) indicating a p type doping. This shifting of the G band position is similar to that reported with changes in the electronic structure and properties of graphene induced by molecular charge transfer in different samples [13]; Single Wall Carbon nanotubes (SWNTs) [14] where charge transfer to bromine and iodine is also known to cause similar shifts of the G band and on the same sample after being contacted by Cr/Au electrodes [15]. Additionally, similar results on the \(I_D\) as a function of \(V_D\) was reported on gas sensors based on FLG with different thickness on the same sample [16], in this case the authors argued that the semiconducting behavior is due to the presence of some defects in the graphene crystal structure caused by the FIB technique at the moment of fabricating their devices. Increasing of the work function in FLG sheets via chloride doping was also recently reported [17].

In order to have a better information of the device, we have measured the output characteristics, fixing the negative (- 40.0 V) and positive (+ 40.0 V) back gate voltage and varying the EVC as shown in Fig. 4(a) and (b). Comparing, Fig. 4(a) and (b) we can see several features on the \(I_D\) current: a) current is more symmetric for negative than for positive gate voltage, b) \(I_D\) increase when the sample is in the presence of \(N_2\) and different EVC, for positive gate voltage, c) positive displacement on the \(I_D\) current for high EVCs (3800 ppm) and negative gate voltage (- 40.0 V), whereas for \(N_2\) and 750 ppm of Eth ID remains almost the same. A proportional displacement of the current with \(V_g\) and \(V_D\) was also reported for three-way electrical gating characteristics of metallic Y-junction carbon nanotubes in an air atmosphere. In this system due to the interconnected nature of the Y junction, the gating is not perfect and there is a current leakage, which is manifested, in the current displacement [18]. However, in the studied device the gate leakage current is in the range of pA, because of, the FLG channel and the gate electrode (substrate) are separated by the 280 nm SiO\(_2\) dielectric, which do not allow passing high gate current from substrate to the graphene channel.

Increasing on the \(I_D\) current, as the positive applied voltage is increased, could be attributed to a reduction of the Schottky barrier height which is unaffected by the presence of \(N_2\) and different ethanol vapor concentrations as shown in Fig. 4(b). On the other hand, modulation of the Schottky barrier by applying positive gate voltage was reported in carbon nanotube field effect transistors-based NH\(_3\) gas sensors [19].
4. Conclusions
In conclusion, we have reported that the Schottky barrier in FLG transistors could be originated from a p-type doping of different areas of FLG sample and could be modulated applying positive and negative back gate voltage in the presence of Air, N₂ and different ethanol vapor concentrations.

5. References
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