1. Introduction

Graphene is a two-dimensional (2D) material that is well known by its remarkable thermomechanical and electronic properties. The ability to modulate and control graphene electronic properties in different and efficient ways are of paramount importance for the commercial realization of graphene applications [1–4]. For instance, graphene field effect transistors (GFETs) have demonstrated great potential for applications in several areas such as high-frequency transistors [2, 5], biological and chemical sensors [6, 7], and in a variety of optoelectronic devices [8–12].

In the GFET configuration, an electric current between the source and drain terminals is modulated by the application of a gate potential [1, 5, 13]. In this context, it is well known in the microelectronics industry that electric transport between the conducting channel and metallic electrodes plays an important role in the device characteristics and performance. Thus, an intensive effort has been devoted to understand and improve the electrical junction between the metallic electrodes and graphene [14–22]. Typically, in a metal–semiconductor junction, there is a Schottky-barrier that actively affects the electronic device properties [20, 21]. However, in a metal-graphene junction, even an Ohmic contact can passively play a role in device conduction due to unusual effects originated from the quantum electronic properties of graphene [23]. Moreover, graphene depicts a zero-gap and approximately linear energy dispersion near the vicinity of the Fermi level [4]. These features provide ambipolar electronic conduction, and GFET transfer characteristics (conductance versus gate voltage.
curves) typically displaying a ‘V-shaped’ form [1]. Thus, the minimum of conductivity (or maximum of resistivity) of the transfer curve corresponds to the crossing of the Fermi level at the Dirac point in the graphene electronic band structure [4]. Around this point, where the graphene density of states vanishes, the concentration of thermoactivated electrons is equal to that of holes being labeled as the charge neutrality point (CNP) [1, 4]. In general, there is only one CNP in the transfer characteristics of GFETs [1, 2]. Nevertheless, several experimental works have demonstrated that graphene devices can exhibit multiple maxima of resistance depending on external environmental conditions, contaminations, and device structuring [24–36]. This means that, in such systems, there are adjacent regions of graphene with different local density of charges, or even the existence of heterojunctions (regions p-type doped nearby regions n-type doped) as it is theoretically predicted [37]. A double-CNP in the transfer curve of a GFET can also be intentionally created using a double-gate structure that enables setting the density of charges at different regions of the graphene channel independently [38–40]. Apart from this case, all the other processes that create the double-CNP are irreversible, which limits the device electrical performance and applicability. Therefore a further understanding of these phenomena, as well as the use of it in a controllable and tunable way is still lacking.

In this work, we systematically investigate how and why molecular hydrogen tunes the electrical properties of graphene devices. We show that the interaction with H2 promotes a local doping of graphene at the metal–graphene interface, which is strongly dependent on the characteristics of the device. For instance, by changing the type of metal–graphene heterojunction, we observe that Ohmic contacts can be strongly or weakly coupled electrostatically with graphene. In a strongly coupled heterojunction, there is a charge-density pinning effect at the metallic leads fixing the charge density nearby. Consequently, GFETs show asymmetric ambipolar conduction, and such asymmetry can be tunable under interaction with molecular hydrogen (H2) [23]. On the other hand, in devices with metallic leads weakly coupled with graphene (such as Au/Cr2O3 electrodes), hydrogen interaction at the metal–graphene interface generates a second CNP in graphene transfer curves (a double-CNP feature). We propose that this double-peak phenomenon arises from the decoupling of the work function of graphene and that of the metallic electrodes under interaction with H2. The induced double-CNP or ‘M-shaped’ form observed is completely controllable and reversible via H2 exposure. Those effects provide considerable electron transfer to graphene layer and large variation in the graphene resistance providing an alternative approach for suitable engineering at metal–graphene interfaces with great potential for application of gas sensors.

2. Experimental methods

For a better understanding of the role of H2 on the electronic properties of GFET, we built several devices with different parameters: device geometry, channel lengths, and types of metallic electrodes. Graphene devices were prepared using monolayer graphene produced via mechanical exfoliation on SiO2(300 nm)/Si substrate, where heavily p-type doped silicon (0.0025 Ω cm) is used as the back-gate electrode [1]. It also is important to mention that before mechanical exfoliation of the graphite crystal, the substrates are cleaned in acetone-bath in an ultrasonic cleaner for 2 min, followed by 2 min in isopropanol and submitted to 50 s of oxygen plasma to ensure better cleaning and adhesion of larger graphene layers. Electron beam lithography and oxygen plasma etching were used to define the graphene shape. The metallic electrodes of all devices were designed by electron beam lithography, followed by thermal metal deposition and lift-off. Here, we fabricated GFETs with pure Au (30 nm), Au/Cr (30 nm/1 nm) and Au/Cr2O3 (30 nm/~1 nm) as metal-type electrodes, forming the metal-type/graphene/SiO2/Si structures. GFETs were also fabricated with 5 nm and 10 nm Cr2O3 thick for the Au/Cr2O3 transistors. In all these devices, the metallic electrodes were defined and deposited on top of the graphene channel, as illustrated in the top panels of figures 1(a) and (c)–(f). However, GFETs were also fabricated by transferring graphene on top of pre-prepared Au/Cr (30 nm/1 nm) electrodes, as illustrated in the top panel of figure 1(b), forming the graphene/Au/Cr/SiO2/Si structures.

Our standard GFETs devices were prepared with several materials as contacts and keeping the same graphene channel length (L = 1 µm), channel width (W = 3 µm), and electrodes length (d = 1 µm). In the inset of figure 2(b) we illustrate the definition of electrode length, d. Additional devices were prepared to investigate the effects of the contact length, graphene channel length, and contact resistance on the formation of secondary CNPs. Accordingly, GFETs with Au/Cr2O3 electrodes, which show tunable secondary CNPs, were prepared at several other configurations: (i) GFETs with several electrodes lengths (from d = 0.25 µm up to d = 2 µm, fixing L = 1 µm and W = 3 µm—see inset in figure 2(b)); (ii) GFETs with several graphene channel lengths (from L = 1 µm up to L = 10 µm, keeping d = 1 µm and W = 3 µm—see inset in figure 2(c)); (iii) GFETs in Hall bar geometry, where we can ignore the influence of contact resistance [17, 23]. In this geometry, we also measure the electronic properties of the device in a non-invasive (figure 1(e)) and invasive (figure 1(f)) configuration [17, 23]. Finally, the formation of the Cr2O3 instead of Cr as a sticking layer underneath the gold contacts was produced by intentional oxidation of the chromium after deposition by thermal evaporation. For this process, immediately after the chromium deposition (~1 nm),...
usually performed at pressures around $2 \times 10^{-6}$ Torr, the thermal evaporation chamber was opened to the environment for 30 min and then pumped down back to $2 \times 10^{-6}$ Torr before the gold deposition. Such an oxidation process of Cr was tested and characterized before we implemented it as our device preparation recipe. The oxidized materials (~1 nm of Cr$_2$O$_3$) were verified by atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) (see supporting information). It is important mentioning that the low adherence of the oxide layer with gold can cause problems during the lift-off process especially for contacts with length $d < 1$ µm. For devices fabricated with electrodes length of $d = 1$ µm or larger, we used a single layer of PMMA 495K-C2, whereas the second layer is composed by 950K-C2. During the lithography process, both layers are exposed at the same dose. However, 495K-C2 is more sensitive at the e-beam exposure, creating the undercut profile. For this case, the total thickness of the double-layer PMMA is around 200 nm, but around 120 nm for the first layer. Then, after metal deposition of around 30 nm of Au/Cr$_2$O$_3$ the samples follow the same procedure as the other samples. After fabrication, each device was inserted into a homemade gas system tube equipped with heater and mass flow controllers, which enables the control of the temperature, from $T = 25$ °C up to $T = 200$ °C, gases flow (Argon (Ar) and H$_2$) with hydrogen concentrations ([H$_2$]), from [H$_2$] = 0.5% up to [H$_2$] = 50% inside the chamber at atmospheric pressure. Before

**Figure 1.** Measurements of two-probe resistance ($R$) as a function of back-gate voltage ($V_G$) under H$_2$ exposure for GFETs with different metal-type electrodes: pure Au/graphene (a), graphene/Au/Cr (b), Au/Cr/graphene (c), and Au/Cr$_2$O$_3$/graphene (d) on top of SiO$_2$/Si substrates. All devices are designed with the same graphene geometry ($L = 1$ µm and $W = 3$ µm) and electrodes length ($d = 1$ µm). (e) Four-probe and (f) two-probe $R \times V_G$ curves for a GFET fabricated in Hall bar geometry with Au/Cr$_2$O$_3$ electrodes. The device in Hall bar geometry was prepared with the channel width of $W = 3$ µm, while the distance between the inner neighboring terminals (channel length) of $L = 7$ µm and the outermost terminals of $L = 15$ µm. All measurements presented in this figure are performed at $T = 200$ °C and the data under [H$_2$] = 20% exposure (red curves) are performed after 1 h of gas exposure, while the black curves are measurements in pure argon, before turning on the molecular hydrogen. The insets in the figures illustrate the metal-type used in the fabrication process, the position of the graphene layer in the GFETs, the device geometry and the configuration for the electrical characterization.
carrying out the electrical measurements, each device undergoes to a thermal conditioning process that consists of keeping the devices at a temperature of $T = 200^\circ C$ under a flow of 300 sccm of ultrapure Ar for 8 h. This process is known to remove absorbed water molecules, impurities and contaminating gases from the graphene surface [41, 42] and other layered materials [43]. For the electrical characterization, we performed mainly two-probe measurements using the standard lock-in techniques, keeping fixed the frequency at 17 Hz and current bias ($I_{SD}$) between the source ($S$) and drain ($D$) terminals of $I_{SD} = 1 \mu A$, while we measured the voltage drop ($V$) in between both electrodes as illustrated in the top panel of figure 1(a). However, for the Hall bar geometry, the same parameters were used in between source and drain, while the voltage was measured in the inner electrodes as illustrated in the top panel of figure 1(e). Finally, for all devices, the total device resistance ($R$) was obtained by applying Ohm’s law.

### 3. Results and discussion

We start by showing typical transfer curves of a GFET and how $H_2$ modifies graphene electrical properties. In figures 1(a)–(d) we present data of two-probe measurements of transfer curves ($R \times V_G$) at $T = 200^\circ C$ of graphene devices with contacts made of Au, Au/Cr and Au/Cr$_2$O$_3$. Note that graphene is contacted with Au electrodes in different ways. In figure 1(a), Au contacts are at the top of graphene, while in figure 1(b), graphene is at the top of the Au electrodes. Firstly, we would like to stress that in all devices characterized graphene main channel are n-type doped. This can be seen by the fact that the CNP locates at negative gate potentials. Such charge transfer effect depends mainly on the activation of surface dangling bonds in the SiO$_2$ by thermal conditioning, which is not controllable, explaining why the CNPs for different devices are not at the same gate voltage [44]. Secondly, the graphene conductance is ambipolar around the CNP, meaning that at the left side of the CNP, the electrical conduction is carried out by positive charge carries (holes) whereas at the right side of the CNP the conduction is executed by negative charge carries (electrons). Moreover, other information can be extracted by asymmetric transfer curves. If the transfer curve shows a larger resistance at the right side of the CNP, graphene at the contact interface is p-type doped promoting a preferential scattering of electrons [14, 17, 23]. Similarly, if the transfer curve shows a larger resistance at the left side of the CNP, the opposite applies, and we can infer that graphene at the contact interface is n-type doped scattering holes more efficiently than electrons.

![Figure 2.](image)
By carefully analyzing figures 1(a)–(d), one can see that there is a preferential scattering of electrons in absence of H\textsubscript{2} (all metallic contacts naturally promote a p-type doping of graphene near the leads). See also the discussion in the supporting information. This statement is more evident in graphene/Cr/Au devices as shown in the black curve of figure 1(c) [14, 17, 23]. However, under exposure to H\textsubscript{2} (red curves in figures 1(a)–(c)), there is an inversion of the asymmetry of the transfer curves [23]. In these circumstances, the metallic contacts promote a n-type doping of graphene in the region near the contacts and resistance at the left side of the CNP is larger than at the right, if one compares the same density of charge. Additionally, under interaction with H\textsubscript{2}, in all devices the CNP shifts towards more negative values of the gate potential, indicating a global electron transfer to the graphene. Previous works have justified similar charge transfer processes via H\textsubscript{2} dissociation and subsequent interaction of the atomic hydrogen with the graphene channel, causing the negative charge transfer and leading to chemical and permanent changes on the GFETs [24, 45]. However, as we will discuss next, we do not observe permanent changes on the graphene electrical properties induced by H\textsubscript{2}, and the idea of a hydrogenation process can be disregarded.

Now, by comparing the results presented in figures 1(a)–(d) it is clear that the CNP shifts (\(\Delta V_G\)) are not the same for all devices. These data indicate that the charge density transferred via interaction with H\textsubscript{2} depends on both the metal-type used and on the electrode position on the graphene channel (top or bottom). In this context, some features can be highlighted. Firstly, the largest charge transfer occurs in graphene devices contacted with pure Au (as we will discuss later, the charge transfer is proportional \(\Delta V_G\)). Secondly, in GFETs with Au/Cr\textsubscript{2}O\textsubscript{3} electrodes, as shown in figure 1(d), in addition to the CNP shift, there is a formation of a second ‘peak’ in the \(I_{SD} \times V_{SD}\) curves when the device is exposed to H\textsubscript{2} (red curve in figure 1(d)), resulting in a ‘M-shaped’ curve. Here, it is important to mention that all data depicted in figures 1(a)–(d) are taken from graphene devices with the same geometry (graphene channel length, width and electrodes length).

Now, we state that all effects discussed above can be addressed to charging effects at the graphene-metallic contact region. A demonstration that the graphene main channel is not becoming charged directly due to an interaction with H\textsubscript{2} is understood in measurements of devices prepared in a Hall bar geometry, as shown in figure 1(e). In such geometry, it is well-known that the contribution from the contact resistances can be disregarded [17, 23]. Indeed, we do not observe any significant charging effect under H\textsubscript{2} exposure, even using Au/Cr\textsubscript{2}O\textsubscript{3} electrodes. A similar result is described in a previous work using Au/Cr electrodes [23]. Nevertheless, when the same device is measured in a two-probe configuration between the nearby terminals (\(L = 7 \mu m\)), the second CNP appears as well as the electron charge transfer, as it is shown in figure 1(f). We emphasize that the double-CNP occurs in all devices while keeping the current bias very low (\(I_{SD} = 1 \mu A\)), suggesting that a second CNP does not appear as a result of charge trapped in the vicinity of the drain at the graphene/SiO\textsubscript{2} interface during a current bias stress [27]. Moreover, we also show in the Supporting Information an investigation of the double-CNP by measuring the hysteresis on the GFETs. Such experiments strongly indicate that contributions from trapped charges at the substrate [27, 28, 47] on the formation of the second CNP and charge transfer can be neglected. In summary, our experiment suggests a strong correlation between the generation of the secondary CNP via charging effects at the metal-graphene interfaces, which also may affect graphene contact resistance.

It is important to address possible changes on the contact resistance when the device is exposed to H\textsubscript{2}. Several works [48–51] propose that tunneling across the metal-graphene interface should dominate the charge injection from the metal into the underlying graphene. Besides that, changes on this transmission probability could result in changes in contact resistance measured, eventually changing the contact behavior from Ohmic to non-Ohmic and also resulting in the observation of multiple CNPs [49, 51]. Therefore, we show in figure 2(a) measurements of \(I_{SD} \times V_{SD}\) for a device with Au/Cr\textsubscript{2}O\textsubscript{3} electrodes before (blue curve) and after (red curve) gas exposure at \(T = 25 \degree C\) and \([H_2] = 20\%\). One can note that the Ohmic behavior (linear relation between \(I_{SD} \times V_{SD}\)) of the device is not affected by the molecules, as expected for the range analyzed. We only note a change on the slope of the curve shown in figure 2(a), which can be associated with the charge transfer to graphene channel, as demonstrated and discussed in figure 1(d). Such linearity implies that the oxide layer deposited does not form any detectable Schottky barrier in our devices. In addition, under interaction with H\textsubscript{2} there is a significant charging effect but the contact region between graphene and Au/Cr\textsubscript{2}O\textsubscript{3} is still Ohmic for any value of gate bias applied (see supporting information). Also, in the Supporting Information, we present the \(I_{SD} \times V_{SD}\) curves for all other devices with different metallic electrodes where a linear response is obtained in all of them (with or without H\textsubscript{2} interaction). We have to mention that in the regime adopted for the realization of the \(I_{SD} \times V_{SD}\) curves, we do not expect to observe any non-ohmic behavior, in accordance to Simmons work [52]. However, if the interaction at the metal-graphene interface would break the H\textsubscript{2} and induce the hydrogenation of the graphene region underneath the contact [53], we believe that, as a consequence of this process, even such small range of voltage bias would bring some distortion in the \(I_{SD} \times V_{SD}\) measured.

Now we investigate how the formation of multiple CNPs under interaction with H\textsubscript{2} depends on the device geometry. It has been reported that the two peaks in
the $R \times V_G$ curves can be associated with the contact area and the length of the graphene channel [34, 36]. In such experiments, the nature of contacts, without the presence of any type of gas, might be causing a local charging effect on the graphene underneath the electrodes. So, in figures 2(b) and (c) we present curves of the resistivity $\rho$ as a function of the carrier density $n$, for devices with several Au/Cr2O3 electrode lengths (figure 2(b)) and graphene channel lengths (figure 2(c)) after H2 exposure. Here, the resistivity is calculated as $\rho = RW/L$, while the carrier density is obtained by $n = C(V_G - V^{\text{CNP}})/e$, where $C$ is the graphene device capacitance per unit area for a 300nm SiO2 thick device, $V^{\text{CNP}}$ is the back-gate voltage value at the first and more positive CNP, and $e$ is the electron charge.

A normalization that considers the CNP at more positive voltage values as $n = 0$ cm$^{-2}$ is adopted to better visualize the phenomenon (secondary peaks). As it will be explained later, such CNP presents the electrostatic conditions needed to neutralize charges at the graphene main channel. Figure 2(b) shows the dependence of the second CNP as a function of the electrode length $d$. Clearly, the second CNP is evident in devices with larger metallic electrodes. Such information is a strong evidence that charge is transferred to graphene underneath the contact, and, very likely, such graphene regions acquire a local charge density that is different from that of the graphene main channel. Moreover, both charge carrier type and density are tunable under conditions needed to neutralize charges at the graphene main channel. However, as soon as H2 corroboration with the hypothesis that the region underneath the contact is important for the interaction with H2 molecules. Note that in this case, the measurements are performed from two neighbor terminals with similar electrodes length $d$, while the graphene geometry is kept fixed at $L = 1 \mu m$ and $W = 3 \mu m$. Hence, any contribution from the graphene area can be neglected.

We also investigate the relationship between the graphene channel $L$ and the appearance of the second CNP in GFETs. In figure 2(c) we present data taken from GFETs with contacts of Au/Cr2O3, with several graphene channel lengths, and under $[H_2] = 20\%$ exposure at $T = 25\ ^\circ C$. In all devices, the length of the contacts is kept fixed at $d = 1 \mu m$ and the measurements are performed from two neighbor terminals for different graphene lengths. From the $\rho \times n$ curves, we see that secondary CNPs are present mainly in short devices: GFETs with small graphene channel lengths. This data corroborates with the hypothesis that in shorter graphene main channels, the contribution of the graphene region underneath the electrodes are more significant [26, 29, 36, 54]. Therefore, we can state that the ratio between the graphene and electrodes length is also important for the observation of multiples CNPs, as it would be expected [36, 48].

A better presentation of the change of the contact resistance ($R_C$) of the devices before and after H2 exposure is shown in figure 2(d). Here, we present data taken from the same device showed in figure 2(c), at a fixed value of $n = -2.8 \times 10^{12}$cm$^{-2}$ (left side of the CNP). The total resistance $R$ scales linearly with $L$, and from the linear extrapolation of the resistance, we can estimate the intercept at $L = 0 \mu m$ which gives the sum of the $R_C$ of both electrodes [48, 49, 55–57]. Average contact resistance is then estimated as half the vertical intercept of the fitting line in figure 2(d). Such values are presented in black, for devices without interaction with H2 ($R_C^{\text{H}_2}$) and, in red, for devices under H2 exposure ($R_C^{\text{H}_2}$). The fitted $R_C$ values are $R_C^{\text{H}_2} = W \cdot (320 \pm 20) \Omega \mu m$ and $R_C^{\text{H}_2} = W \cdot (540 \pm 40) \Omega \mu m$, respectively. Therefore, one can notice that the GFETs exposed to H2 depict higher contact resistance, indicating that $R_C$ is affected by the hydrogen molecules, $R_C^{\text{H}_2}/R_C^{\text{H}_2} \approx 169\%$. We also show in the Supporting Information the analysis of contact resistance for values at the right side of the CNP in figure 2(c). One can note that a similar behavior is observed with a change in $R_C$ and a decrease of the contact resistance of about $R_C^{\text{H}_2}/R_C^{\text{H}_2} \approx 93\%$ after hydrogen exposure. These results suggest that H2 molecules can significantly change the metal-graphene interface potential. For instance, we believe that such molecules modify the p-n junctions at the metal-graphene regions, therefore changing the preferential scattering mechanisms (asymmetry in the transfer curves), as previously discussed. In other words, changes in the doping level at the metal-graphene interface define the preferential scattering for either holes or electrons, modifying then the contact resistance measured. Consequently, this phenomenon explains the increase observed for $R_C^{\text{H}_2}$ for the left side of CNP (hole-branch) and decrease for the right (electron-branch) side.

Next, we present in more detail how the electrical response of a GFETs with Au/Cr2O3 electrodes evolves from single CNP to multiple CNPs. Figure 3(a) shows the time evolution of the second CNP when the device (with $d = 1 \mu m$) is exposed to $[H_2] = 20\%$ at $T = 200\ ^\circ C$. Initially, under an Argon atmosphere (without H2), the $R \times V_G$ curve depicts only one CNP at $V_{ch} = -7.6\ V$, which we label it as the CNP position for the graphene channel. However, as soon as there is H2 inside the chamber (process of H2 adsorption), the electron charge transfer takes place ($V_{ch}^H$ shifts to more negative values $V_{ch}^H = -13.7\ V$) and a second CNP emerges at $V_{ch}^H = -37\ V$, reaching a stationary state after 30 min under gas exposure. We label such new maximum of resistance as the CNP position for the graphene underneath the electrodes. After we turn off the H2 gas (process of H2 desorption), the system evolves to the initial stage showing a single CNP (figure 3(b)). It is important to stress that the interaction of the device with molecular hydrogen is completely reversible. For measurements under $[H_2] = 20\%$ the desorption time is larger than 1.5 h. We also need to emphasize that the desorption depends on the length $d$ of the electrodes: decreasing its length also decreases the desorption...
time. For instance, the desorption time drops down from 5 h for a length of \( d = 2 \, \mu m \) to 0.5 h for \( d = 0.5 \, \mu m \). This effect is consistent with the diffusion of H\(_2\) molecules in between the graphene sheet and the electrodes, indicating that the trapped molecules can easily escape from narrower metallic contacts.

It is important mentioning that such times (adsorption and desorption) are related with the evolution of the double-CNP. It means the time needed to obtain a fixed position for both CNPs (adsorption) and to restore the initial condition (desorption). However, by performing experiments of total resistance as a function of exposure time at a fixed gate voltage and gas concentration, one can note that the saturation time (time needed to reach 90% of the maximum/minimum resistance values) interestingly shows a different time frame (see supporting information).

We also note that the saturation time also decreases for contacts with longer lengths. For \( d = 2 \, \mu m \), for example, the saturation time is about 3 min, while for \( d = 0.5 \, \mu m \) it is 8 min. Such non-expected behavior is still not clear to us and this process is under new studies because manipulation and control over the device time evolution are crucial for providing a faster route to detect molecular hydrogen using metal-type engineering in GFETs.

Even though the data presented in figures 3(a) and (b) correspond to a temperature \( T = 200 \, ^\circ C \), the same behavior occurs for temperatures ranging from \( T = 25 \, ^\circ C \) up to \( T = 200 \, ^\circ C \). For instance, figure 3(c) shows \( R \times n \) curves for all temperatures analyzed after 1 h under \([H_2] = 20\%\) exposure. One can note that the appearance of the second CNP does not depend on the temperature: even at \( T = 25 \, ^\circ C \) there is the formation of the second CNP. The fact that the second CNP can be observed at room temperature, but with a very small charge transfer process with H\(_2\) exposure (see supplementary information), would indicate that both phenomena are in fact decoupled from each other, having different origins as we will discuss later. Moreover, from figure 3(c) it is possible to observe an increase in the splitting between the CNPs as the temperature increases, which is also presented in more detail in figure 3(d). In this figure, we show the Fermi energy variation (\( \Delta E_{\text{Fermi}} \)) calculated between both CNPs as a function of temperature. In this case, the Fermi energy variation is defined by \( \Delta E_{\text{Fermi}} = \hbar \nu_F \sqrt{\frac{\pi}{|\Delta n|}} \), where \( \hbar = 6.58 \times 10^{-16} \, \text{eV s}^{-1} \) is the Planck’s constant \( (\hbar/2\pi) \), the Fermi velocity is given by \( \nu_F = 1 \times 10^6 \, \text{m s}^{-1} \) and \( |\Delta n| \) is the difference of the amount of charge density in between both CNPs [33, 34]. In this figure, one can note that the splitting in energy increases up to \( T = 150 \, ^\circ C \) and decreases afterwards for \( T = 200 \, ^\circ C \). The initial increase of the splitting with temperature indicates that the interaction at the metal-graphene interface is favored at higher temperatures, showing that modifications at the metal-graphene interface by H\(_2\) molecules are thermally activated. In addition, the \( \Delta E_{\text{Fermi}} \) decrease at 200 \( ^\circ C \) might be related to a possible thermal induced partial reduction of the chromium oxide. Additionally, the splitting between both CNPs is also dependent on the H\(_2\) concentration. In figure 3(e) we present the \( R \times n \) curves for all concentrations analyzed (from \([H_2] = 0.5\% \) up to \([H_2] = 50\%\)) and after 1 h under H\(_2\) exposure at \( T = 200 \, ^\circ C \). This result shows that both the intensity of the second CNP and the splitting between both CNPs depend on the H\(_2\) concentration, see figure 3(f). This indicates that the amount of H\(_2\) at the interface is determinant.

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**Figure 3.** \( R \times V_G \) curves for different time of exposure to \([H_2] = 20\%\) in argon during adsorption (a) and desorption (b) processes at \( T = 200 \, ^\circ C \). (c) \( R \times n \) for different temperatures, which the measurements are obtained after 1 h under exposure to \([H_2] = 20\%\). (d) Variation of Fermi energy (\( \Delta E_{\text{Fermi}} \)) between both CNPs as a function of temperature. (e) \( R \times n \) for different \([H_2]\), where the measurements are obtained after 1 h at \( T = 200 \, ^\circ C \). (f) \( \Delta E_{\text{Fermi}} \times [H_2] \) at \( T = 200 \, ^\circ C \). All the measurements presented in this figure are performed on a GFET fabricated with Au/Cr\(_2\)O\(_3\) electrodes and contact length of \( d = 1 \, \mu m \).
for the definition of the doping level at the region underneath the electrodes. One may note a difference in the $\Delta E_{\text{Ferm}}$ between figures 3(d) and (f) for the case of $[\text{H}_2]=20\%$. We discuss such difference due to a sample dependence because both measurements were taken in two different devices. Note that even though the samples were fabricated following the same process and with similar graphene and electrodes sizes, some parameters are not totally controllable. For instance, defects on substrate surface, some residues in between the metal-graphene interface coming from the sample manipulation or irregularities on the metal deposition and lift-off. Nevertheless, we must point out that independently of such difference, similar behavior for both temperature and hydrogen concentration dependence was observed for all devices measured.

Now, it is important to stress that apart from a double-gate structure that enables setting of the density of charges at different regions of the graphene channel independently, all the other processes that create a double-CNP are irreversible [18, 26, 28, 30, 33, 34]. In our case, the formation of the second CNP is totally controlled and reversible in devices fabricated with a 1nm thick layer of Cr$_2$O$_3$ and under hydrogen exposure. However, if the GFETs are fabricated with 5nm or 10nm of Cr$_2$O$_3$, the second CNP is presented even before H$_2$ gas exposure but are also tunable under H$_2$ interaction (see the supporting information). In such conditions, when the devices are exposed to H$_2$ there is a shift of both CNPs towards more negative gate values, indicating that both regions (graphene main channel and graphene underneath the contacts) accept electrons. We shall also comment that GFETs with thick layers of Cr$_2$O$_3$ are extremely unstable at high temperatures whereas devices fabricated with 1nm Cr$_2$O$_3$ thick are very stable.

We will now address possible explanations for the phenomenology associated to H$_2$ doping. Let us first consider possible physical mechanisms for the n-doping action of H$_2$ molecules on an Au-graphene interface, without the presence of either Cr or Cr$_2$O$_3$, as evidenced by the results of figure 1(a). Our discussion will be based on existing theoretical first-principles results on the literature, as well as on previous experimental evidence. A detailed first-principles study of electronic and structural properties of interfaces between graphene and the (111) surfaces of Al, Ag, Cu, Au, and Pt has been performed in the works of Giovannetti et al and Khomyakov et al [22, 58]. The first-principles results show that the shift of the CNP of graphene with respect to the Fermi level, $\Delta E_F$, is an increasing monotonous function of the metal-graphene distance for all interfaces. For the Au-graphene case at the equilibrium distance, the calculation shows graphene as p-type doped, with $\Delta E_F$ of 0.19 eV. Therefore, an increase of this distance due to the presence of an H$_2$ interlayer would result in additional p-doping, and not n-doping, from geometrical reasons alone. The calculations also show a positive and monotonic dependence of $\Delta E_F$ with $W_M - W_G$, where $W_M$ and $W_G$ are the work functions of the isolated metal surface and graphene, respectively. Among the investigated systems, the ones closest to the neutrality condition ($\Delta E_F = 0$) are Au and Cu, with Au being slightly p-dopant ($\Delta E_F = 0.19$ eV) and Cu being slightly n-dopant ($\Delta E_F = -0.17$ eV). The calculated work functions $W_M$ of the Au and Cu surface are respectively 5.54 eV and 5.22 eV. From our measured n-type carrier density of the order of $2 \times 10^{12}$ cm$^{-2}$ under hydrogen exposure, we can estimate, from the electronic density of states of graphene, that $\Delta E_F = -0.16$ eV, very similar to the calculated value for Cu. We therefore estimate that the net action of H$_2$ exposure is to reduce the work function $W_M$ of Au by order of 0.3 eV and consequently transform the graphene doping from p-type to n-type. Are there known experiments involving H$_2$ adsorption that could lead to reductions of the Au surface work function $W_M$ by tenths of an eV? The answer is ‘yes’ for Au–TiO$_2$–Ti diodes used as high sensitivity H$_2$ sensors [59]. In this work, the Ohmic behavior of the Au–TiO$_2$ junction in hydrogen atmosphere was associated to a reduction of the Au surface work function by several tenths of an eV. This information can, in principle, provide a possible mechanism for a negative charge transfer from non-planar regions of Au to graphene in the presence of adsorbed H$_2$.

Now, let us discuss the formation of the second CNP based on the literature. Previous works [14, 26, 28, 51] discussed the observation of multiple CNPs when the charge-density pinning induced by the electrodes is weak. Hence the graphene underneath the contact can be modulated by gate bias, resulting in changes of the charge density between both regions. Moreover, at the conditions of weak metal-graphene interaction, the conical points in the graphene band structure are preserved, but charge transfer to or from the metallic electrodes can take place, modulating then the Fermi level at the oxide surface. Therefore, we might be facing two distinct mechanisms for H$_2$-induced n-doping, one associated to Au-graphene (as discussed in the preceding paragraphs) and the other associated to chromium oxide-graphene. The latter H$_2$-doping mechanism has been proposed to involve the modification of the oxide surface [60]. We suggest that this mechanism might also result in the decoupling of the electron states of graphene from those of the oxide contact regions. Such decoupling has been considered a necessary ingredient.
for the appearance of two CNPs in $R \times V_G$ curves of GFETs with Ni contacts due to the oxidation of Ni at contact regions [26, 29, 36], and such $R \times V_G$ curves are similar to the one observed in figure 1(d) upon H$_2$ exposure, suggesting a similar physical origin.

Finally, figure 4 illustrates a phenomenological model for the different metal/graphene heterojunctions studied. Figure 4(a) shows that effect of the molecular hydrogen when only Au metallic contacts are used. In this case, the $R \times V_G$ curve shows only one CNP and the asymmetry generated by the p-type doping induced by the Au-electrodes and pinning of the graphene work function by the metal [14, 22, 50]. In this case the Fermi energy ($E_F$) level for the region underneath the contact remains fixed, while the $E_F$ for the graphene channel can be tunable by the gate bias. However, we suggest that the H$_2$ molecules modify the interface potential by interacting with Au interface reducing its work function and causing the observed n-type doing effect. Now, figure 4(b) depicts the case of GFETs with Au/Cr electrodes without H$_2$ exposure, where the $R \times V_G$ curve also shows a single CNP and asymmetry induced by the electrodes and pinning of the graphene work function [14, 22, 50]. Moreover, similar to the case of pristine gold, the $E_F$ for the region underneath the contact remains fixed, while the $E_F$ for the graphene channel can be tunable by the gate bias. In this case, when the hydrogen is turned on, the $R \times V_G$ curve presents a single CNP, and a subtle n-type doping, as illustrated in figure 4(b). Nevertheless, solely for GFETs with Au/Cr$_2$O$_3$ electrodes, the $R \times V_G$ curves present two CNPs when the hydrogen is turned on, as we illustrate in figure 4(c). Such observation can be associated to the decoupling of the work functions between the metal and graphene that occurs induced by the presence of H$_2$ molecules at the metal-graphene interface. In the latter case, the $E_F$ of both regions are modulated by the gate bias, and if both regions exhibit different doping levels, the $R \times V_G$ curve shows double-CNP, one of them originated from the minimum of density of states in the graphene channel and the other coming from the graphene at the contact region.

Figure 4. (a) A schematic of the graphene device with hydrogen exposure for GFETs with Au metallic electrodes. The band diagram on the contact region indicates the charge-density pinning ($E_F$ fixed) induced by the metallic electrode, and the band diagram on channel region shows the $E_F$ modulation by the $V_G$ application. The $R \times V_G$ curve presents only one CNP associated solely with the graphene channel. (b) A schematic of the graphene device with gas exposure for GFETs with Au/Cr metallic electrodes. The $R \times V_G$ curves present also the charge-density pinning ($E_F$ fixed) before and after H$_2$ exposure. (c) A schematic of the graphene device with gas exposure for GFETs with Au/Cr$_2$O$_3$ metallic electrodes. The band diagram of the graphene underneath the contact and at the channel regions show the $E_F$ modulation by the gate bias, demonstrating now the existence of double-CNP in the $R \times V_G$ curve.
4. Conclusion

In summary, we have investigated the formation of multiple CNPs induced in graphene devices by molecular hydrogen exposure. Our findings demonstrate that the observation of the ‘M-shape’ on the $R \times V_G$ curves obtained by using thin layers of chromium oxide as metal-type electrodes is not solely dependent on the graphene channel and electrodes size, but also on hydrogen concentration and the temperature at which the interaction occurs. Moreover, our study confirms that the formation of the second CNP is totally reversible and indicates that after H$_2$ exposure the graphene regions underneath the electrodes can be modulated by the gate bias. Therefore, our results are valuable for two reasons: first, for a better understanding of the metal–graphene interface and the formation of multiple CNPs; second, it shows that the electrode engineering can be used to improve the hydrogen detection using non-functionalized graphene devices.

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ORCID iDs

AR Cadore https://orcid.org/0000-0003-1081-0915
H Chacham https://orcid.org/0000-0001-5041-9094
LC Campos https://orcid.org/0000-0001-6792-7554
RG Lacerda https://orcid.org/0000-0003-4777-7370

References

[1] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV and Firsov AV 2004 Electric field effect in atomically thin carbon films Science 306 666–9
[2] Novoselov KS, Fal’ Ko V, Colombo L, Gellert P R, Schwab M G and Kim K 2012 A roadmap for graphene Nature 490 192–200
[3] Ferrari A C et al 2015 Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems Nanoscale 7 4598–810
[4] Castro Neto AH, Peres NM R, Novoselov KS, Geim AK and Guinea F 2009 The electronic properties of graphene Rev. Mod. Phys. 81 109–62
[5] Schwierz F 2010 Graphene transistors Nat. Nanotechnol. 5 487–96
[6] Zhan B, Li C, Yang J, Jenkins G, Huang W and Dong X 2014 Graphene field-effect transistor and its application for electronic sensing Small 10 4042–65
[7] Yan F, Zhang M and Li J 2014 Solution-gated graphene transistors for chemical and biological sensors Adv. Healthcare Mater. 3 313–31
[8] Wang F, Zhang Y, Tian C, Girit C, Zettl A, Crommie M and Shen Y R 2008 Gate-variable optical transitions in graphene Science 320 206–9
[9] Li J, Niu L, Zheng Z and Yan F 2014 Photosensitive graphene transistors Adv. Mater. 26 5239–73
[10] Bonaccorso F, Sun Z, Hasan T and Ferrari A C 2010 Graphene photonics and optoelectronics Nat. Photon. 4 611–22
[11] Barcelos ID et al 2018 Infrared fingerprints of natural 2D Talc and plasmon–photon coupling in graphene–talc heterostructures ACS Photonics 5 1912–8
[12] Maiti P C B et al 2019 Anisotropic Flow Control and Gate Modulation of Hybrid Phonon–Polaritons Nano Lett. 19 708–15
[13] Ardito F M, Mendes-de-Sá T G, Cadore A R, Gomes P F, Mafra D L, Barcelos ID, Lacerda R G, Ikawa F and Granado E 2018 Damping of Landau levels in neutral graphene at low magnetic fields: a phonon Raman scattering study Phys. Rev. B 97 035419
[14] Song S M and Cho B J 2013 Contact resistance in graphene channel transistors Carbon Lett. 14 162–70
[15] Song S M, Park J K, Sul O J and Cho B J 2012 Determination of work function of graphene under a metal electrode and its role in contact resistance Nano Lett. 12 3887–92
[16] Low T, Hong S, Appenzeller J, Datta S and Lundstrom M S 2009 Conductance asymmetry of graphene p–n junction IEEE Trans. Electron Devices 56 1292–9
[17] Huard B, Stander N, Sulpizio J A and Goldhaber-Gordon D 2008 Evidence of the role of contacts on the observed electron-hole asymmetry in graphene Phys. Rev. B 78 1–6
[18] Peng S, Jin Z, Zhang D, Shi J, Niu J, Huang X, Yao Y, Zhang Y and Yu G 2018 How do contact and channel contribute to the Dirac points in graphene field-effect transistors Adv. Electron. Mater. 4 1800158
[19] Wang J et al 2013 One-dimensional electrical contact to a two-dimensional material Science 342 614–7
[20] Giubileo F and Di Bartolomeo A 2017 The role of contact resistance in graphene field-effect devices Prog. Surf. Sci. 92 143–75
[21] Schulman D S, Arnold A J and Das S 2018 Contact engineering for 2D materials and devices Chem. Soc. Rev. 47 3037–58
[22] Giovannetti G, Khomyakov P A, Brocks G, Karpan V M, Van Den Brink J and Kelly P J 2008 Doping graphene with metal contacts Phys. Rev. Lett. 101 026803
[23] Cadore A R, Mania E, de Morais E A, Watanabe K, Taniguchi T, Lacerda R G and Campos L C 2016 Metal–graphene heterojunction modulation via H2 interaction Adv. Mater. 28 5933–109
[24] Park M, Yun Y J, Lee M, Jeong D H, Yun J, Park Y W and Kim B H 2015 Local doping of graphene devices by selective hydrogen adsorption Adv. Mater. 27 51720
[25] Brenner K and Murali R 2010 Single step, complementary doping of graphene Appl. Phys. Lett. 97 7–10
[26] Nouchi R and Tanigaki K 2010 Charge-density depinning at metal contacts of graphene field-effect transistors Appl. Phys. Lett. 96 1–4
[27] Chiu HY, Perebeinos V, Lin Y M and Avouris P 2010 Controllable p–n junction formation in monolayer graphene using electrostatic substrate engineering Nano Lett. 10 4634–9
[28] Di Bartolomeo A, Giubileo F, Santandrea S, Romeo F, Citro R, Schroeder T and Lupina G 2011 Charge transfer and partial pinning at the contacts as the origin of a double dip in the transfer characteristics of graphene-based field-effect transistors Nanotechnology 22 225702
[29] Nouchi R and Tanigaki K 2015 Competitive interfacial charge transfer to graphene from the electrode contacts and surface adsorbates Appl. Phys. Lett. 106 083107
[30] Sun Y, Xie D, Zhang C, Li X, Xu J, Sun M, Teng C, Li X and Zhou H 2017 Poly (ethylene imine)–modulated transport behaviors of graphene field effect transistors with double Dirac points J. Appl. Phys. 121 113405
[31] Yu X, Shen Y, Liu T, Wu T and Jie Wang Q 2015 Photocurrent generation in lateral graphene p-n junction created by electron-beam irradiation Sci. Rep. 5 12014

[32] Jqbal M Z, Anwar N, Siddique S, Jqbal M W and Hussain T 2017 Formation of p-n junction with stable n-doping in graphene field effect transistors using e-beam irradiation Opt. Mater. 69 234–8

[33] Zhang C, Xie D, Xu J-L, Li X-M, Sun Y-L, Dai R-X, Li X and Zhu H-W 2015 HfO2 dielectric thickness dependence of electrical properties in graphene field effect transistors with double conductance minima J. Appl. Phys. 118 144501

[34] Feng T, Xie D, Xu J, Zhao H, Li G, Ren T and Zhu H 2014 Back-gate graphene field-effect transistors with double conductance minima Carbon 79 363–8

[35] Di Bartolomeo A, Santandrea S, Giubileo F, Romeo F, Petrosino M, Gitro R, Barbara P, Lupina G, Schroeder T and Rubino A 2013 Effect of back-gate on contact resistance and on channel conductance in graphene-based field-effect transistors Diam. Relat. Mater. 38 19–23

[36] Nouchi R and Tanigaki K 2014 Path of the current flow at the metal contacts of graphene field-effect transistors with distorted transfer characteristics Appl. Phys. Lett. 103 033112

[37] Barraza-Lopez S, Vaněvić M, Kindlemann M and Chou M Y 2010 Effects of metallic contacts on electron transport through graphene Phys. Rev. Lett. 104 1–4

[38] Williams JR, DiCarlo I and Marcus C M 2007 Quantum Hall effect in a gate-controlled p-n junction of graphene Science 317 638–41

[39] Campos L C, Young A F, Surakatiborn K, Watanabe K, Taniguchi T and Jarillo-Herrero P 2012 Quantum and classical confinement of resonant states in a trilayer graphene Fabry–Pérot interferometer Nat. Commun. 3 1236–9

[40] Wang J X, Huang Q Q, Wu C L, Wei Z J, Xuan N N, Sun Z Z, Fu Y Y and Huang R 2015 Realization of controllable graphene p-n junctions through gate dielectric engineering RSC Adv. 5 80496–500

[41] Silvestre I, De Morais E A, Melo A O, Campos L C, Goncalves A M B, Cadore A R, Ferlauto A S, Chacham H, Mazzoni M S C and Lacerda R G 2013 Asymmetric effect of oxygen adsorption on electron and hole mobilities in bilayer graphene: Long- and short-range scattering mechanisms ACS Nano 7 6597–604

[42] Cadore A R, Mania E, Alencar A B, Rezende N P, de Oliveira S, Watanabe K, Taniguchi T, Chacham H, Campos L C and Lacerda R G 2018 Enhancing the response of N83 graphene-sensors by using devices with different graphene-substrate distances Sensors Actuators B 266 638–46

[43] Rezende N P et al 2018 Probing the electronic properties of monolayer MoS2 via interaction with molecular hydrogen Adv. Electron. Mater. 5 1800591

[44] Romero H E, Shen N, Joshi P, Gutierrez H R, Tadigadapa S A, Solo J O and Eklund P C 2008 n-type behavior of graphene supported on Si/SiO2 substrates ACS Nano 2 2037–44

[45] Kim B H et al 2012 N-type graphene induced by dissociative H2 adsorption at room temperature Sci. Rep. 2 690

[46] Hong S J et al 2013 Verification of electron doping in single-layer graphene due to H2 exposure with thermoelectric power Appl. Phys. Lett. 106 142110

[47] Cadore A R, Mania E, Watanabe K, Taniguchi T, Lacerda R G and Campos L C 2016 Thermally activated hysterisis in high quality graphene/h-BN devices Appl. Phys. Lett. 108 233101

[48] Nouchi R 2017 Contact resistance at planar metal contacts on bilayer metal contacts and effects of molecular insertion layers Nanotechnology 28 134003

[49] Xia F, Perebeinos V, Lin Y M, Wu Y and Avouris P 2011 The origins and limits of metal-graphene junction resistance Nat. Nanotechnol. 6 179–84

[50] Peng S, Jin Z, Zhang D, Shi J, Zhang Y and Yu G 2017 Evidence of electric field-tunable tunneling probability in graphene and metal contact Nanoscale 9 9520–8

[51] Karnatak P, Sai T P, Goswami S, Ghatak S, Kaushal S and Ghosh A 2016 Current crowding mediated large contact noise in graphene field-effect transistors Nat. Commun. 7 13703

[52] Simmons J G 1963 Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film J. Appl. Phys. 34 1793–803

[53] Elias D C et al 2009 Control of graphene’s properties by reversible hydrogenation: evidence for graphene Sci. 323 610–3

[54] Nouchi R, Saito T and Tanigaki K 2011 Determination of carrier type doped from metal contacts to graphene by channel-length-dependent shift of charge neutrality points Appl. Phys. Express 4 035101

[55] Nagashio K, Nishimura T, Kita K and Toriumi A 2009 Metal-graphene contact as a performance Killer of ultra-high mobility graphene analysis of intrinsic mobility and contact resistance 2009 IEEE Int. Electron Devices Meeting (IEEE) pp 1–4

[56] Russo S, Craciun M F, Yamamoto M, Morpurgo A F and Tanrucha S 2010 Contact resistance in graphene-based devices Physica E 42 677–9

[57] Nouchi R, Saito T and Tanigaki K 2012 Observation of negative contact resistances in graphene field-effect transistors J. Appl. Phys. 111 084314

[58] Khomyakov P A, Giovannetti G, Rusu P C, Brocks G, Van Den Brink J and Kelly P J 2009 First-principles study of the interaction and charge transfer between graphene and metals Phys. Rev. B 79 1–12

[59] Rahbarpour S and Hossein-Babaei F 2011 Hydrogen detection with noble metal-TiO2 Schottky diodes Key Eng. Mater. 495 289–93

[60] Miremadi B K, Singh R C, Chen Z, Roy Morrison S and Colbow K 1994 Chromium oxide gas sensors for the detection of hydrogen, oxygen and nitrogen oxide Sensors Actuators B 21 1–4