Correlation of low frequency noise characteristics with the interfacial charge exchange reaction at graphene devices

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ABSTRACT

Graphene based low noise amplifier has been studied actively because the noise characteristics of graphene devices are known to be superior to those of silicon devices. However, 1/f noise characteristics of graphene grown by chemical vapor deposition (CVD) may increase by an order of magnitude when measured before the charge exchange reaction at the interface of the graphene and substrate is saturated. Based on the close correlation between the level of low frequency noise signal and fast charge exchange reaction (in milliseconds), the conductivity fluctuation of graphene caused by the interfacial charge exchange reaction may be the source of the increased low frequency noise. This result suggests that the current assessment of noise characteristics is too optimistic for graphene and that the defect density of CVD graphene needs to be further reduced to minimize the charge exchange reaction.

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1. Introduction

Although graphene is known to have many electrical advantages over silicon, such as high mobility, high current drivability, and noise immunity, it has been unclear how the graphene can be practically used in electronic applications without a band gap [1]. A low noise amplifier has therefore been suggested as the first feasible device application for the graphene because it is less sensitive to off-state leakage current [2].

Studies of intrinsic noise characteristics of exfoliated graphene have found that its Hooge parameter ($\alpha_H \sim 10^{-3}$) is lower than that of silicon devices ($\alpha_H \sim 10^{-3}$) and that the noise source of graphene device is primarily related to its resistance and the interface charge trapping between the graphene and the dielectric, which causes the graphene channel mobility to fluctuate [3–9]. The 1/f noise of single-layer graphene (SLG) showed the highest level at a Dirac point where the carrier concentration is minimal, but was more than ten times lower than the typical 1/f noise level of silicon [7,10]. On the other hand, bilayer graphene shows a maximal noise level at the Dirac point due to a band gap generated by an external electric field. In both cases, graphene’s low frequency noise was thought to originate with charge trapping.
Graphene field-effect transistors (FETs) were fabricated with CVD graphene devices were annealed in high vacuum (10^{-7}\text{Torr}) for 30 min at 200 \degree C to recover symmetrical \( \mu \text{C} \) to \( \mu \text{C} \). Current understanding on the 1/f noise characteristics of graphene is primarily relying on the test procedures developed for silicon device, but the impacts of defects, substrate and other graphene specific surface reactions on the test methods itself has not been considered yet.

Furthermore, early studies of the noise characteristics of graphene focused on exfoliated graphene [4–7]; CVD graphene, however, had not been studied in detail. Even though CVD graphene is a more practical material for integration, its electrical defect density is still high and its noise characteristics are expected to be worse than exfoliated graphene.

This paper presents the results of an investigation of the 1/f noise characteristics of CVD graphene before and after the saturation of the transient interfacial charge exchange reaction to determine whether the low frequency noise level is affected by this interfacial charge exchange reaction.

2. Experiments

Graphene field-effect transistors (FETs) were fabricated with CVD SLG on a 100 nm SiO_{2}/Si substrate [15]. 100 nm Au electrodes were deposited using an e-beam evaporator and patterned using contact lithography and a wet etch with gold etchant TFA (TRANSENSE product) at room temperature. Graphene channels, which were divided into 3–6 \mu m wide and 1–5 \mu m long strips, were patterned with an oxygen plasma etch. The graphene channel region was selectively passivated with 30 nm of Al_{2}O_{3} dielectric grown by atomic layer deposition (ALD) at 130 \degree C to recover symmetrical \( \mu \text{C} \)–\( \mu \text{C} \) characteristics [16]. Dirac points (\( V_{\text{Dirac}} \)) were then shifted to around \(-10\) V from \(+20\) V, indicating negatively charged contaminants such as hydroxyl adsorption were successfully reduced [13]. For a backside contact, 50 nm Au was deposited after etching off a native oxide layer. Before electrical measurements, the graphene devices were annealed in high vacuum (\(-2 \times 10^{-7}\) Torr) for 30 min at 200 \degree C to obtain more intrinsic device characteristics [16].

The low frequency noise measurement system consisted of a dynamic signal analyzer (Agilent 35670A) and a low noise current preamplifier (LNA, Stanford Research SR570). The SR570 is also used as a source of drain bias for graphene FET measurements, as shown in Fig. 1 [17–20]. In this measurement, external noise peaks due to the vibration of probe tips and the harmonics of the AC power signal at 60, 120 Hz, and so on are often included, which may hinder the comparison of noise signals. In this work, extensive precautions were taken to perform the measurement with minimal external noises [21]. Ground lines were directly connected to an earth ground to avoid a ground loop. The LNA was powered with an internal battery, while the dynamic signal analyzer was connected to the AC power (220 V, 60 Hz). All equipment was manually operated to eliminate external computer noises through a GPIB connection. The entire system was placed in a Faraday cage to shield the interference due to external electromagnetic waves. In addition to the most stringent precautions against well-known external noise sources, noises radiating from the electronic equipment within the Faraday cage were also reduced. The influences of the charge coupled device (CCD) module, power cable, and anti-vibration table were examined and unnecessary components were powered off and even disconnected from the power line during the measurements. The influences of these components are shown in Fig. 2a–c. As a result, almost all of the extrinsic noise peaks were successfully suppressed in our measurement as shown in Fig. 2d [21].

Finally, 1/f noises of graphene FETs were measured at \( V_{g} = V_{\text{Dirac}} \), \( V_{\text{Dirac}} + 20 \) V and \( V_{\text{Dirac}} + 50 \) V, respectively, with 50 mV of drain bias. Different gate biases were used to examine the noise characteristics at different background carrier concentrations, i.e., at different channel resistance levels. \( V_{\text{Dirac}} \) was used as a reference point because the 1/f noise is most pronounced at the charge neutrality point (CNP). The positive bias region with a reference to \( V_{\text{Dirac}} \) was used to investigate the properties of the electron conduction branch.

3. Results and discussion

In general, low frequency noise measurements in the 1 to 1000 Hz range use internally averaged data to minimize the data fluctuation; a typical test can take several minutes. On the other hand, charge trapping-like mechanisms causing hysteretic current–voltage characteristics can occur on various time scales, from microseconds to a few thousand seconds. While the hysteretic behavior of graphene devices is often attributed to charge trapping, it would be more accurate to describe this as a charge exchange mechanism that includes chemical processes generating charge complexes such as OH⁻ around the graphene layer by charge exchange [22]. If the low frequency noise is primarily due to a random charge fluctuation through a tunneling mechanism with a characteristic 1–1000 Hz frequency, the saturation of the charge exchange mechanism should not affect the low frequency measurement. However, if the charge exchange mechanism

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**Fig. 1 – Schematic set-up of low frequency noise measurement. Dashed line for GND is a shield with metal tube to prevent interactions with external noise. Stanford Research SR570 is the low noise amplifier.**
observed in a graphene device can also affect low frequency noise characteristics, they will be different before and after saturation. Also, some of the noise measurement results reported in the literature may have been too optimistic because the influence of interfacial charge exchange reactions may have been excluded in the measurements.

This problem is likely to be even more significant in CVD graphene, which has a higher defect density than exfoliated graphene because the chemical reaction and adhesion of water is enhanced at the defect sites [23,24]. In this work, low frequency noise characteristics were measured at different time intervals after applying a gate bias. For a fast measurement, the averaging time was minimized to finish the measurement within 30 s (resolution = 1600, bandwidth = 1600 Hz, and averaging number = 30 in dynamic signal analyzer set up), while measuring the reference took several hundred seconds. In this way, data fluctuation may increase slightly, but the accuracy of the data does not significantly degrade. A criterion of 30 s was chosen considering the limitations of the test system and the typical time scale of charge exchanges.

The normalized current power spectral density ($S_f$) curves of graphene devices measured within 30 s and after 30 s under a constant voltage bias at the $V_{D\text{irac}}$ and $V_d = 50$ mV are shown in Fig. 3. The dashed lines represent data collected within 30 s of applying the gate bias; the solid lines represent data collected after applying the gate bias for 30 s to ensure that the charge exchange mechanism was fully saturated. Both cases show an average slope ($a$) around $-0.9$, but the $1/f$ noise measured within 30 s was approximately ten times higher than those measured after 30 s. This result implies that previous research may have underestimated the noise level of graphene by missing the noise signals that appear active during only the first few tens of seconds.

To understand the charge exchange mechanism that was active during the first 30 s of operation, temporal behaviors of the charge exchange mechanism must be studied. Several
previous studies addressed the hysteretic characteristics of graphene devices with different voltage sweep rates or directions to show qualitative differences using exemplary I–V curves shown in Fig. 4a. However, the amount of charge exchange reaction at a given bias and specific time scale cannot be quantitatively analyzed in this way because the trapping and charge exchange strongly depend on the electric field applied to the graphene and surrounding dielectric.

In this work, a single bias pulse with a short rise and fall time was used to quantify the transient charge trapping at a given overdrive bias ($V_g - V_{\text{Dirac}}$) [20]. The rise and fall times were 1 ms while the pulse was 10 ms. In this way, the amount of charge trapping during 10 ms at a constant gate bias could be quantitatively measured. Note that this method cannot capture fast trapping that occurs within 1 ms rise time. To do so, pulses with extremely short rise and fall times would be needed to eliminate a potential error due to the fast trapping and saturation within 1 ms. Even though the pulse I–V measurement system itself is designed to capture trapping within 50 ns, the impedance of the graphene device used in this work is too high to apply such a short pulse. To reduce the impedance, a short channel device with a gate length less than 100 nm should be used. Since we are primarily dealing with low frequency noises from 1 to 1000 Hz and physical processes that are active for milliseconds, a 10 ms pulse with 1 ms rise time is sufficient. The interference from such a fast transient charge exchange is currently assumed to be minimal.

Fig. 4b is a pulse $I_d$–$V_g$ curve. The hysteresis generated under constant voltage for 10 ms is shown as $I_d$ drops at a fixed gate bias while the I–V curves are measured during the rise and fall time. Fig. 4c shows the amount of hysteresis over time. Current decreases rapidly in the first few milliseconds. This kind of current drop can be modeled with an exponential function and a characteristic time constant $t = \exp(-kt)$ [25]. Fig. 4d extends the time scale from a few milliseconds to 110 s to show the long-term saturation behavior. The decreased $I_d$ shown in Fig. 4d slowly saturated over 4.07 ms, and the current drop is almost negligible after 30 s [25]. This is why 30 s was chosen for the measurement shown in Fig. 3.

These kinds of transient and hysteretic behaviors have often been attributed to charge trapping in the substrate or other sites near the graphene. While it is possible to have progressive charge trapping with a long time constant in a deep trap site in SiO$_2$, this charge trapping is unlikely to be reversible within milliseconds as shown in Fig. 4a. Also, tunneling cannot explain the millisecond time constant because typical tunneling is much faster than milliseconds [25]. In terms of the time scale and reversibility, the behaviors observed in this work may be similar to characteristics of negative bias temperature instability (NBTI) in SiO$_2$ [26]. However, graphene does not have dangling bonds like silicon to hold and release

Fig. 4 – Drain current of back gate graphene FETs ($W = 2 \mu$m, $L = 5 \mu$m) measured at $V_g - V_{\text{Dirac}} = +20$ V from 1 ms to 120 s. (a) DC $I_d$–$V_g$ curves showing the hysteresis curve with a gate bias sweep direction in sequence of 0 V → 50 V → −50 V → 0 V. (b) The pulse $I_d$–$V_g$ curve with a rise/fall time = 1 ms, pulse duration = 10 ms. (c) The $I_d$ curve vs. pulse duration showing the current reduction due to charge generated outside of graphene. (d) $I_d$ curve vs. time curve, combining pulse I–V and DC IV curve on a time scale from 1 ms to 11 ms for a pulse I–V and from 5 ms to 120 s for DC IV.
hydrogen atoms; therefore NBTI cannot contribute to this behavior.

Thus, the origin of the charge exchange mechanism with the 4.07 ms time constant and reversible characteristics cannot be explained by the charge trapping/detrapping model. The most plausible mechanism for this kind of behavior in the graphene might be a chemical redox process \((\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH})\) because the chemical process can be reversible and occurs roughly on the order of milliseconds to seconds [22–25,27–29]. Since the generation of hydroxyl bonds in carbon complexes such as diamond and carbon nanotubes has been studied before, such reaction in graphene is not surprising [24,27]. Negatively charged hydroxyl bonds (OH\(^-\)) can induce positive charges in the graphene channel and reduce the electron concentration, i.e., conductivity, under a positive bias. Thus, the fluctuation in conductivity caused by the redox reaction can be correlated with the increased level of low frequency noise [4]. A more detailed description of the interfacial reaction mechanism is beyond the scope of this paper and will be published elsewhere [22].

The reduction in current, \(\Delta I\), due to charge generated during the 10 ms pulse is correlated with \(V_{\text{Dirac}}\) shift as shown in Fig. 5. \(\Delta I\) under a constant bias stress is linearly proportional to \(\Delta V_{\text{Dirac}}\) and the number of charge traps \((n = C_{\text{ox}} \Delta V_{\text{Dirac}}/q)\) [25]. The relationship between \(\Delta I\) and \(\Delta V_{\text{Dirac}}\) is essentially linear as expected from \(\Delta I = \Delta Q/\Delta t = C_{\text{ox}} \Delta V/\Delta t\); i.e., the charge generated outside the graphene shifts the Fermi level of the graphene, directly affecting the electron concentration. As expected from this data, the low frequency noise level at 10 Hz correlates well with \(\Delta I\) as shown in Fig. 6. When more charge is generated, represented by the higher \(\Delta I\), the low frequency noise level also increases. This is why the noise level measured within 10 ms is ten times higher than the noise level measured after 30 s. This result also indicates that when the charge exchange reaction is fully saturated, only a minimal reverse reaction contributes to the low frequency noise level. This reduction in noise after the saturation of \(\Delta I\) change, i.e., a saturation of the interfacial reaction, results in underestimating the low frequency noise level, as was done in previous studies of graphene devices that used a slow measurement method with several hundred seconds of test time [11,13,14]. Also, the quality of graphene is closely related to the level of noise because the charge exchange reaction can be easily activated through broken bonds in the graphene.

4. Conclusions

Low frequency noise characteristics of graphene channel devices were found to correlate with the amount of current reduction from chemical processes that generate charges around the graphene channel rather than with charge trapping through tunneling as suggested by previous work. The fluctuation of the Fermi level due to charge generation and reduction appears to be the major source of increased low frequency noise. As a result, graphene devices exhibit 1/f noise about ten times higher when the generation of transient charges is not saturated.

This work implies that device operation within milliseconds to a few seconds can be influenced by enhanced 1/f noise-like behaviors. Furthermore, intrinsically good 1/f noise characteristics may possibly be achieved by minimizing the source of such extrinsic chemical reactions.

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