LOW-FREQUENCY ELECTRONIC NOISES IN CVD GRAPHENE GAS SENSORS

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ABSTRACT
This paper reports the investigation of low-frequency noise (1/f noise) in the Polyethylenimine (PEI) doped graphene gas sensor based on the architecture of using chemical vapor deposition (CVD) to make a graphene field effect transistor (GFET). Compare to the state-of-art, three advancements have been achieved: (1) first demonstration of 1/f noise characterization in PEI doped CVD graphene FET sensor under nitrogen, water, ethanol and methanol vapor environments; (2) modeling the measured 1/f noise characteristic features through simulating random charge transfer events caused by gas adsorption-desorption processes on graphene surface; (3) rejection of the complex background noise through an advanced digital signal processing method to accurately obtain the 1/f noise in graphene FET gas sensors. As such, the noise characterization, modeling and signal processing method on CVD-grown graphene FET gas sensors could provide new guidelines for researchers to develop 1/f noise based high performance gas sensing devices for practical applications.

KEYWORDS
Graphene gas sensor, Graphene FET, Low-frequency noise, 1/f noise

INTRODUCTION
Graphene has unique material properties because of its two-dimensional nature and extremely stable covalent bonds. Owing to the weak van der Waals interaction and specific scattering mechanisms when exposed to chemicals, graphene is promising to deliver low baseline drift and high sensitivity gas sensing solutions at room temperature [1]. In recent years, low-frequency electronic noises on graphene-based gas sensors, especially the characteristics of signal fluctuations, have been reported as potential sensing parameters to increase the graphene gas sensing sensitivity, selectivity, fidelity and recovery speed as compared to the conventional time-domain material resistive sensing parameters [2-4]. The shaping effects of various chemical vapors on the low-frequency noise spectrum of mechanical exfoliated graphene FET have been experimentally and theoretically demonstrated in the past [5-7]. However, such validation hasn’t been applied to graphene FET sensors made from CVD processes graphene for volume productions. Here, we report the research of gas sensing effect using signal low-frequency fluctuations on gas sensors based on CVD-grown graphene with PEI as the sensitized dopants.

In this work, a lock-in measurement method was used to fetch the resistance fluctuation of a CVD grown graphene FET with PEI doping, and several post signal processing techniques include oversampling, time domain digital filtering and frequency domain adaptive filter are adopted to resolve the characteristic 1/f noise under complex background noises. Based on this method, we found a gate voltage dependence and chemical vapor sensitive spectrum of the 1/f noise in the as-fabricated graphene FET gas sensor, qualitatively in agreement with our simulation results. Interestingly, we observed large change of the 1/f noise after the injection of chemical vapors, yet the characteristic Lorentz bulge in the 1/f noise (1-1000 Hz) as reported previously in the mechanically-exfoliated graphene FET gas sensors [4] did not show up in our CVD graphene FET gas sensors.

We organize this paper in the following manner. Firstly, the preliminary concept and fundamentals of the low-frequency noise gas sensors are introduced. Secondly, the fabrication of the GFET sensor and setup of the in-situ gas measurement system are presented. Last, the digital signal processing method and measurement results are presented and discussed. This section also compares the 1/f noise characteristic of the CVD-grown graphene FET sensor with mechanically-exfoliated graphene FET gas sensors.

GAS SENSING BASED ON LOW-FREQUENCY NOISE OF GFET
GFET gas sensors are well known to be operated based on the change of channel resistance due to surface charge transfers. As shown in Figure1, a gas molecule on the top surface of graphene becomes a positively charged impurity after donating electrons from its molecular orbital to graphene. The charged impurity scatters the carriers in long-range manner or short-range manner depend on different situations. Low-frequency fluctuation of mechanical exfoliated GFET graphene has been researched in details [4]. However, many questions still exist as to which of the two mechanisms is the main cause of low-frequency noise in mechanically-exfoliated GFET devices: (1) mobility fluctuations due to charged scattering centers on substrate and device surface; (2) number density fluctuations due to charged impurities on the surface of the device or on the substrate.
Figure 1. Schematic diagram of the graphene FET(GFET) gas sensing (monolayer graphene on a 300nm SiO2 /Si wafer) mechanism by means of charge transfer.

We simulate the overall processes of gas molecules absorption and desorption on graphene surface for three kinds of gas with different absorption time, desorption time and live time (tapped time with trap state) from one single molecule to 1000 molecules. Figure 2 shows the simulation results explaining the sensitivity of low-frequency noise during the gas sensing process. From the power spectral density simulation result (Figure 2c), 1/f characteristic of gas sensing can be clearly observed.

![Figure 2](image)

Figure 2. Theoretical model of gas molecules adsorption and desorption process (a) Model of the adsorption and desorption behaviors of one single gas molecule on graphene surface. The time constants of the process vary with each kind of gas molecules. (b) Simulation results of the noises contributed by random adsorption and desorption of 1000 molecules on graphene surface. (c) Normalized power spectral density of the simulated noises in frequency domain.

FABRICATION AND MEASUREMENT SETUP

The monolayer graphene grown via the CVD method was transferred onto a silicon substrate with a 300nm SiO2 thermally grown. The graphene layer was then patterned by lithography and oxygen plasma etching (10s, 50W) to define the channel of the graphene FET. The electrical contacts were evaporated by Pd/Au (3nm/30nm) and patterned using the lift-off process to define the source and drain electrodes. The graphene surface was rinsed with PEI solution (20% w.t. in H2O) to tune the Dirac point around 0V to maximized gas sensitivity (Figure 3a). The gas sensor was then diced and wire bonded to a customized printed circuit board (PCB1, Figure 3b) and sealed in a small plastic chamber (10mL, Figure 3c). The measurement terminals and sensors multiplexer switches were designed in the bottom printed circuit board (PCB2, Figure 3d). The optical photo of the integrated GFET gas sensor testing setup was also shown in Figure 3d. All fabrication processes were carried out in the Marvell Nanofabrication Laboratory at UC Berkeley.

![Figure 3](image)

Figure 3. a) Layout and optical microscopy image of the microfabricated, back-gated four-terminal GFET sensors used for the gas sensing tests (scale bar 10um) with a total of four sensors on each die. b) Sensor packaged and bonded on a customized printed circuit board. C) Schematic of the gas sensor test setup. d) The picture of gas sensor test setup.

The resistance fluctuation of the GFET gas sensor was measured by the alternating current (AC) lock-in technique which can simultaneously measure both sensor resistance fluctuations and background noise compared with the direct current (DC) lock-in method [3]. The instrument control and gas measurement process were automatically executed by a MATLAB program. The low-frequency noise measurement setup for the AC lock-in measurement techniques is shown in Figure 4. Time constant of the lock-in amplifier was set to 100 micro seconds. This gives a measurement bandwidth of 1.6 kHz. The sampling rate of the data acquisition (DAQ) card was set to 100kHz considering the Nyquist sample theorem. Frequency of the source (Vs) was kept higher than the measurement bandwidth. The source-drain current IDS was biased to 1µA which is sufficiently small to avoid the current induced effects such as electro- migration with a carrier frequency...
significantly higher than the upper cutoff frequency of the noise measurement bandwidth. To achieve better frequency resolution in the frequency domain, the time series of resistance fluctuations were recorded in ten contiguous segments of 100 s each. The stream mode of the data acquisition card was employed to realize the high-capacity data acquisition, transmission and high-efficiency storage.

**RESULTS AND DISCUSSION**

The measurement system was enclosed in an aluminum box to lower the electrical interferences coming from the environment. However, the low frequency measurement result is still not clean because of complex environmental noises (Figure 5a). Therefore, several comprehensive digital signal processing (DSP) methods are employed, including oversampling, digital filtering in time domain and frequency domain adaptive filter and the Welch’s averaged periodogram method with Blackman-Harris window is used to obtain the power spectral density (PSD) (Figure 5b). After that, the PSD plots become much cleaner than the original ones and most noisy spectrums coming from the environment are eliminated except the power frequency spectrum (60 Hz and its odd times frequencies) from the power lines.

**Figure 6** shows a typical noise spectral density \( S_V(f) \propto 1/f^\gamma \) with experimental parameter \( \gamma = 1.21 \) (here \( V \) is the voltage between the source and drain electrode). The measurements were performed at room temperature. The noise spectral density was determined for the source-drain currents set at 1 µA. The noise spectrum was collected for the four-terminal device to lower the contact noise from contact resistance. At the same time, Figure 6 illustrates the noise spectral density measured in nitrogen with high dependency with applied gate voltage from -40 V to 40 V. The \( 1/f \) spectrum was indicated with the dashed line.
mechanical exfoliated graphene FET graphene devices as an interesting sensing parameter [6-9]. Some gases induce bulges at characteristic frequencies in the spectral density of the low-frequency resistance fluctuations to indicate the selectivity of different chemical vapors. In order to test the same approach for CVD FET graphene, we measured the low frequency noise spectral density exposed to nitrogen and chemical vapors at room temperature. We tested the noise power spectral density of GFET in nitrogen and other chemical vapors. For testing the sensor operations, nitrogen gas (flow rate at 200 standard cubic centimeters per minute) was utilized to produce the chemical vapors by bubbling corresponding chemical solvents and diluting the gas flow. The data were acquired at the same gate voltage ($V_g=0V$) and source-drain current (1 μA) for each case. The change of the noise spectra was found as a result of the exposure to the different vapors. It is found that the low-frequency part of spectra has good noise spectra measurements but there is no trace of bulge for any chemical vapors. This is in a striking contrast to mechanically-exfoliated graphene FET devices. As such, low frequency noise is a better selectivity parameter for mechanically-exfoliated graphene. The main reason may originate from the CVD fabrication process which may produce cavities and defects on graphene due to external contaminations or the substrate effects; and dangling bond at the edge of the graphene due to the etching process [10-11]. Another reason may come from the process of lithography and etching which can result in additional defects on graphene. These problems can cause gas molecule trapping and releasing from the defects found on the graphene and then lead to the absence of bulge. However, the low frequency fluctuations of resistance can still be used for chemical vapor sensing. In the prototype tests, we also found variance of noise power spectral when exposed to different amounts of water vapor ranging from relative humidity (RH) 1%-90%. Different level of noise power spectral with differ density of water vapor can be clearly observed.

CONCLUSION

In conclusion, we demonstrate the low-frequency noise gas sensing results coming from CVD graphene FETs. We used alternating-current lock-in measurement techniques and adopted advanced signal processing method include oversampling, digital filtering in time domain, and the frequency domain adaptive filtering to achieve the low-frequency noise in complex experimental environments. Based on this method, we found that the low frequency fluctuations of gas sensor exposure to ethanol, methanol, and water vapors can have 1/f noise dependence with large changes in the frequency domain. At the same time, the gas molecules adsorption-desorption model is in good agreement with the experimental results. However, the characteristic Lorentz bulge in 1/f noise (1-1000 Hz) as reported previously in mechanically-exfoliated graphene FET gas sensors did not show up in our experimental results.

REFERENCE


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