Sensitive detection of water/oxygen molecule adsorption and reaction on a titanium oxide nanosheet with a graphene field effect transistor

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Abstract

We have investigated molecule adsorption phenomena on a chemically active surface of titanium oxide nanosheet by coupling with an electrically sensitive graphene field effect transistor (FET). Super-hydrophilic surface of the titanium oxide nanosheet forms a water-layer in ambient air which exhibits a large hysteresis of drain current in the hybrid FET for sweeping gate-voltage. The large hysteresis disappears in vacuum, which indicates physically adsorbed water molecules on the surface of the titanium oxide nanosheet dominantly contribute to the hysteresis. UV light irradiation in vacuum significantly changes the drain current due to desorption of the adsorbed molecules. Sufficient UV irradiation results in symmetric gate-voltage dependence similar to those of conventional graphene FETs. Exposure to an oxygen gas atmosphere leads to a heavy hole doping in the FET, where the binding of the oxygen molecules is stronger than that of water molecules. In a humidified nitrogen atmosphere, a large shift of charge neutrality point is observed in transfer characteristics crossing between electron doping and hole doping. By contrast, a clear square-shaped hysteresis loop is observed in a humidified oxygen atmosphere, where the hole density in the graphene drastically changed with O₂/H₂O redox couple reaction on the titanium oxide nanosheet.

1. Introduction

Discovery of graphene has opened the door to novel approaches for fundamental research and device application on two-dimensional (2D) systems [1–3]. Various types of 2D materials reveal specific physical and chemical properties corresponding to the structures and the electronic states [4, 5]. Furthermore, hybrid structures combining different 2D materials each other show novel functionalities and are applicable for future flexible devices [6, 7]. Due to their large surface/volume ratio, 2D materials are extremely sensitive to the surface conditions and their surroundings [8, 9]. For the case of graphene field effect transistor (FET) on SiO₂/Si substrate, charge impurities in SiO₂ and surface roughness suppress the mobility of graphene. Water molecules adsorbed on the graphene or trapped at the interface between the graphene and the SiO₂ cause a hysteresis in FET characteristics [10, 11]. To overcome such problems, graphene FETs encapsulated in hexagonal boron nitride (h-BN) were fabricated and exhibited extremely high electron/hole mobilities [12–14]. Control of surface and interface in devices built by 2D materials are important issues comparing with conventional devices fabricated from bulk materials.

In various types of 2D materials, we focus on chemically exfoliated titanium oxide nanosheet (TN). TNs with thickness of 1 nm are obtained from layered titanate and have a large lateral size, typically several microns [15, 16]. Bulk titanium oxides, so-called rutile and anatase, show characteristic surface phenomena such as...
super-hydrophilicity and UV photo-catalysis. Since they are essential materials for various fields, a large number of surface science studies related with titanium oxides have been reported \cite{17, 18, 19, 20}. In ambient air, it is well known that water molecules and oxygen molecules are adsorbed on surface of titanium oxides. The adsorption behaviors are dependent on vacancies and surface structures in the oxides. TNs also show the characteristic surface phenomena similarly in bulk titanium oxides \cite{21, 22}. Titanium/oxygen vacancies in TNs have also been investigated experimentally \cite{23, 24} and theoretically \cite{25, 26}. In our earlier works, we found a large humidity dependence of proton transport in a water-layer formed on a TN \cite{27}. We also found a suppression of photocurrent due to adsorption of oxygen molecules in a photo-diode with TN under UV illumination \cite{28}. The results indicate that water/oxygen molecules are adsorbed on the surface of the individual TN similarly in bulk titanium oxides. In the present study, we fabricate a graphene/TN hybrid FET structure, where adsorptions of molecules strongly affect the FET characteristics. Pristine graphene is chemically inert, mainly detects molecules attached with surrounding materials (e.g., substrate and surface contamination). Indeed, resist residues on a graphene unexpectedly enhance the sensor response \cite{29}. Hence, we can expect that hybridizations with other chemically sensitive 2D materials drastically improve the sensitivity of molecule adsorptions on the hybrid structures. In our device, a highly conductive graphene enables us to sensitively reveal the characteristic surface phenomena on the TN coupled with the graphene. In this paper, we report adsorption of water/oxygen molecules in a graphene/TN hybrid FET and desorption under UV irradiation and compare a reference pristine graphene FET. To our best knowledge, this is the first report of a graphene FET stacked with a chemically sensitive 2D metal oxide. The result promisingly opens the way to future chemical sensors composed of graphene and chemically sensitive 2D materials.

2. Sample fabrication

First, graphene flakes were mechanically exfoliated from a highly ordered pyrolytic graphite (HOPG) by using a Scotch tape and were transferred to SiO2/Si substrate. The thickness of the SiO2 is 300 nm. Next, TNs chemically exfoliated from layered titanate crystals by the same method as in previous works \cite{30, 31} were stacked on the exfoliated graphene flakes by using the Langmuir-Blodgett technique \cite{32} as shown in figure S1(a) (available online at stacks.iop.org/NANOX/1/030022/mmedia). For removing organic residues, the sample was annealed in Ar(95%)/H2(5%) atmosphere at 400 °C for 6 h. The single layer TNs deposited on the SiO2/Si substrate are visible and distinguishable from few-layer TNs by an optical microscope similarly in graphene [29]. As shown in figure S1(b), one few-layer graphene is fully covered with one large TN. An atomic force microscopy (AFM) image in figure S1(c) reveals the stacking condition in detail. Although some wrinkles and cracks are observed, TN is closely adhered to the few-layer graphene. The measured thickness of the few-layer graphene by AFM is about 1 nm, which indicates bi- or tri-layer graphene exists under the TN in this sample. Two-terminal electrodes were fabricated by electron beam lithography on the TN/graphene hybrid structure as shown in figure S1(d). The electrode gap is about 1.5 μm.

3. Results and discussion

Figure 1 shows a schematic illustration of the hybrid FET device with the channel length $L \approx 1.5 \mu m$ and the channel width $W \approx 1.5 \mu m$. Since the TN shows insulating behavior \cite{32}, a current flows dominantly into the graphene. The contact resistance with contact area $\approx 1 \mu m^2$ due to the insertion of the TN between the graphene and the metal electrode is expected to be below 1 kΩ. In graphene/h-BN hybrid structures, the area-normalized

\begin{figure}[h]
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\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Schematic illustration of the graphene/TN hybrid FET device.}
\end{figure}
contact resistances due to monolayer of h-BN are about 1 kΩ\(\mu\)m\(^2\) [30]. The energy band gap of TN is smaller than that of h-BN, so that smaller contact resistances in graphene/TN hybrid structures are expected. A drain current \(I_D\) was measured by a source meter under constant bias voltage \(V_D = 10\) mV for all measurements. A back-gate voltage \(V_G\) was applied between the highly doped Si substrate and the source electrode. A pristine graphene FET with the channel length \(L \approx 1.5\) \(\mu\)m and the channel width \(W \approx 0.5\) \(\mu\)m was also prepared as a reference.

Figure 2(a) shows the drain current as a function of back-gate voltage. In ambient air (relative humidity \(= 60\%\)), we observed a large hysteresis due to adsorption of water molecules. After this measurement, sample space was evacuated in 1 h until the pressure is less than \(10^{-5}\) Torr. The hysteresis disappears in the vacuum condition as shown in figure 2(a). Similar hysteresis behaviors were observed in graphene FET samples with SiO\(_2\)/Si substrate [10, 11]. Since water molecules which cause the hysteresis are trapped at the interface between the graphene and the substrate, the hysteresis is not easy to eliminate by a simple evacuation in the most cases. Figure 2(b) shows the transfer characteristics of the reference graphene FET. The observed hysteresis was smaller than that of the graphene/TN hybrid FET and still remained even in vacuum. By contrast, a relatively short evacuation diminished the hysteresis in the graphene/TN hybrid FET. The result implies that physically adsorbed water molecules on the surface of TN, which are easily removed by evacuation, mainly cause the observed large hysteresis in the hybrid FET.

The slope of the drain current for sweeping gate voltage in vacuum is negative, which indicates a p-type (hole) conduction occurs in the hybrid FET device. Since TN is a wide gap semiconductor with much less conductivity, holes in the graphene dominantly contribute to the drain current. For achieving photo-induced desorption of adsorbed molecules, UV irradiation (wavelength: 254 nm, amplitude: 2 mW cm\(^{-2}\)) in vacuum
was carried out in 2 days. After the sufficient irradiation, the current in the hybrid FET became insensitive to a switching of UV irradiation and showed ambipolar FET characteristics with electron-hole asymmetry \[31, 32\] as shown in figure 2(a) similar to those of typical graphene FETs. Neglecting the contribution of the contact resistances, the electron and hole mobilities are roughly estimated from the FET characteristics \[1\] by the following equation,

\[
\mu \approx \frac{1}{C_G W V_D} \left| \frac{dI_D}{dV_G} \right|
\]

Here, \(C_G = 115 \, \mu F \, m^{-2}\) is the gate capacitance per area for the graphene/SiO\(_2\)(300 nm)/Si structure. The electron and hole mobilities in the graphene/TN hybrid FET after the UV irradiation are 200 cm\(^2\)/Vs and 400 cm\(^2\)/Vs, respectively. These values are much smaller than those of the reference graphene FET \(\approx 3,000\) cm\(^2\)/Vs, which indicates that the coupling with the TN suppresses the carrier mobility in the graphene.

In order to elucidate the molecule adsorption effect, especially water and oxygen, the change in the drain current at zero gate-voltage \(V_G = 0\) V was monitored when the sufficiently UV irradiated sample was exposed into various gas atmospheres as shown in figure 3(a). Dry N\(_2\) exposure did not cause a sudden change although a gradual small shift in the current was observed. The small shift may originate from a small amount of gas molecules remained in the vacuum chamber even after the evacuation. By contrast, dry O\(_2\) exposure significantly increased the current, which indicates that oxygen molecules adsorption on the TN causes a heavy hole doping in the graphene. Similar behaviors have been observed in the graphene/TiO\(_2\) hybrid FETs \[33, 34\]. In those works, it is argued that oxygen anions adsorbed on titanium oxides play an important role in the UV response of the hybrid devices. Wet N\(_2\) (bubbling dry N\(_2\) gas through water bath) exposure increased the current comparing with the case of dry N\(_2\), which indicates adsorption of water molecules also generates electron/hole in the graphene. The current in wet O\(_2\) reaches the highest value in the different types of gas exposure measurements.

\[\text{Figure 3. Time dependence of drain current in the graphene/TN hybrid FET (a) and the reference graphene FET (b) exposed to dry N}_2\ (green), to wet N\(_2\) (blue), to dry O\(_2\) (red), and to wet O\(_2\) (magenta) after sufficient UV irradiation in vacuum.}\]
Control experiments in a pristine graphene FET reveals the high sensitivity of molecule adsorptions in the hybrid FET. The relative current change $\Delta I/I_0$ due to molecule adsorptions after UV cleaning increases from about 10% in the pristine graphene FET up to about 300% in the hybrid FET.

After the each gas exposure, we monitored the photo-response in the hybrid FET with respect to switching of UV light irradiation for clarifying desorption of adsorbed molecules as shown in figure 4. As a reference, we checked the photo-response of the sufficiently UV irradiated sample in vacuum. We could not observe any obvious changes in the current, which implies that electron-hole pairs excited by the UV irradiation don’t directly contribute to the current in the hybrid device. Significant photo-current was observed in a graphene FET with a passivation layer of 30 nm Al$_2$O$_3$ after UV cleaning [35]. In our hybrid device, molecule adsorptions on the thinner TN strongly affect the graphene conduction, however, the contribution of photo-current is negligibly small. In the case of dry N$_2$ exposure, the slightly increased current quickly recovered to the value before the exposure. By contrast, a continuous response to switching of UV light irradiation was clearly observed in the case of dry O$_2$ exposure. The current decreased due to desorption of oxygen molecules induced by UV light, and gradually increased when the UV light was turned off. In the case of wet N$_2$ exposure, a significant response was also observed. Chemical adsorption of water molecules leads to formation of hydroxyl groups on the surface of TN. In our first-principle simulation, it is predicted that hydroxyl radicals are released from the surface of TN under UV light irradiation [24]. It implies that the observed current change originates from formation and release of hydroxyl groups in wet N$_2$ atmosphere. Interestingly, the current in wet O$_2$ atmosphere gradually increased with repeated switching of UV irradiation. A mixture of water and oxygen molecules is expected to grow a surface structure with super-hydrophilic character under UV irradiation. Further studies are needed for understanding the mechanism of super-hydrophilic character in detail.

After the each UV switching measurement, we evacuated the sample space and then monitored desorption of molecules under continuous UV irradiation in vacuum as shown in figure S2. In the case of dry N$_2$ and wet N$_2$ gas exposure, the current decreased and quickly became a stable value in a few minutes. The result implies that hydroxyl groups are relatively easy to remove from the surface of TN. By contrast, it takes a quite long time to remove strongly bound oxygen molecules from the surface of TN. Especially in the case of wet O$_2$ exposure, desorption of molecules slowly proceeded in 3 days.

Finally, we focus on the hysteresis of drain current with respect to gate-voltage sweeping due to adsorption of water molecules. Figure 5(a) shows the FET characteristics in wet N$_2$ ambient for different settings of sweeping range. Comparing with the result in ambient air as shown in figure 2, we can observe a charge neutral point normally appeared in conventional graphene FETs. Hysteretic gate-voltage characteristics are frequently observed in various types of FET under conditions surrounded by water molecules [36–38]. In wet N$_2$ ambient, a physically adsorbed water-layer is formed on the surface of super-hydrophilic TN, which causes the large hysteresis. The hysteresis loop clearly depends on the sweeping range. For sweeping the gate voltage up to +50 V, the current increased with gradual electron-doping in the presence of water layer. Reversing the sweeping direction to negative at +50 V, the current suddenly decreased and reached to the minimum (charge neutrality point) at +43 V and gradually increased with hole-doping. Reversing the sweeping direction to positive at −50 V, the current suddenly decreased again. The sudden drops in the current by reversing the sweeping direction...
also occurred for the sweeping between +100 V and −100 V. In the case of wet O₂, a large hysteresis also appeared as shown in figure 5(b). Charge neutrality point was not observed even for sweeping the gate voltage up to +100 V. Similar large p-type hysteresis behaviors have been reported in carbon nanotube FETs [36, 39]. In these works, it is discussed that the hysteresis is caused by electrochemical doping of O₂/H₂O redox couple [39–42]. In our sample, we can conclude that water and oxygen molecules adsorbed on the surface of TN induce the electrochemical redox reaction and subsequent charge transfer between the TN and the graphene reveals the observed large hysteresis.

4. Conclusions

We have investigated adsorption of water/oxygen molecules on a graphene/TN hybrid FET, where the electrically sensitive graphene reveals subsequent charge transfer due to the molecule adsorption on the chemically active surface of the 2D crystalized metal oxide. Water molecules adsorbed on the super-hydrophilic surface induce a large hysteresis of gate-voltage characteristics of the FET due to O₂/H₂O redox couple reaction. Adsorption of oxygen molecules causes a heavy hole doping as previously observed in graphene FETs. UV light irradiation in vacuum removes the adsorbed molecules which are origins of carrier doping in the graphene, and then appears ambipolar FET characteristics.

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