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In situ Tuning of Bandgap in Graphene Oxide Achieved by Solid State Ionics Device

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Abstract

In situ tuning of the sp^2/sp^3 fraction in graphene oxide (GO) has been developed based on electrochemical reduction and oxidation (redox) reaction caused by ion migration in a solid state electrolyte. The reversible variation of the GO sp^2/sp^3 fraction in all solid state device was evidenced by both transport property modulation and a variation in the optical band gap.

1. Introduction

GO has attracted much attention as a material for exploring a variety of physical properties, e.g. variable band gap, wide energy range of photoluminescence (PL), room temperature ferromagnetism and so on.[1-4] The uniqueness of GO originates from electronic disorder due to sp^3 hybridization carbon, which bonds mainly with oxygen atoms, in sp^2 conjugated networks. The sp^2/sp^3 fraction positively correlates with the carbon/oxygen ratio (C/O), and it dominantly affects the band gap. It should be possible to tune the various properties of GO in situ by adjusting the sp^2/sp^3 fraction, which is usually controlled chemically (e.g., through reaction with hydrazine, $NaBH_4$, and so on), by thermal annealing, or by plasma treatment. While these methods generate sufficient variation in the sp^2/sp^3 fraction to modulate the physical properties, they cannot be used for in situ tuning, which provides excellent multifunctional devices with both variable energy PL emission and variable ferromagnetism in addition to transparent, ultrathin, flexible and low cost. In this contribution, we report in situ tuning of the sp^2/sp^3 fraction based on redox reaction achieved by an all-solid-state electric double layer (EDL) transistor with a multilayer GO and yttria stabilized zirconia (YSZ) proton-conductor.[5]

2. Experimental

Electrochemical measurement

An all-solid-state EDL transistor (EDLT, shown schematically in Fig. 1) was fabricated on the flat surface of a SiO_2 substrate. A 5.0-mg/ml GO aqueous solution containing one- atomic-layer GOs with a dimension of several hundred nm^2, was spin-coated onto the substrate and dried in air at 333 K for 1 hour. A 700-nm-thick YSZ thin film was deposited by pulse laser deposition (PLD) using a sintered 10%YSZ target pellet with 99.9% purity at oxygen pressure of 10 Pa. The substrate was kept at room temperature during the PLD process. Electrochemical measurements were performed using a Keithley 4200-SCS parameter analyzer

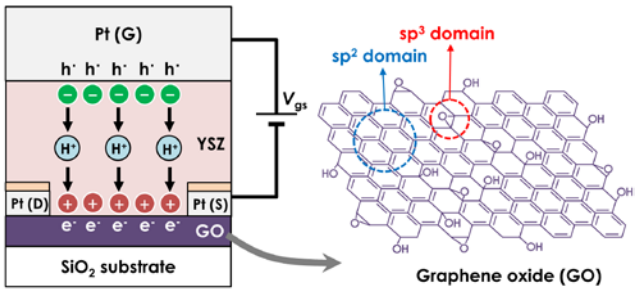

Fig. 1 Schematic illustration of GO-based EDLT with YSZ proton conductor with positive V_{gs} applied condition..

UV-Vis-NIR reflectance measurement

A two-terminal cell with an indium tin oxide (ITO) transparent electrode/GO/YSZ/Pt multilayer structure was fabricated for UV-Vis-NIR reflectance measurement. First, dc bias was applied for ten minutes and the bias was off. After ten minutes, the spectra were measured without dc bias application.

3. Results and discussion

Electrochemical measurement

The upper panel in Fig. 2 plots the electrical conduction characteristics (i_d vs. V_{gs}) at room temperature of an EDLT gated by proton migration in YSZ. In contrast to the drastic variation in i_d for air, the variation for vacuum was minimal. The relatively large i_g for air is attributed to an EDL charging current at the GO/YSZ interface and to a GO electrochemical reaction. The absence of i_g in vacuum corresponds to the removal of the physisorbed water molecules from the YSZ and the resultant decrease in proton conductivity. Thus proton migration in the YSZ clearly plays crucially important role in i_{ds} modulation.

The EDLT exhibited an abrupt jump in i_d, from less than several tenth of a pA to μA order at V_{gs} of 2.1 V in air (indicated as (a) in Figure 2). Furthermore, i_d increased when V_{gs} was swept toward 0 V (indicated as (b)). These modulations resulted in huge differences in the i_d (as large as six orders of magnitude) between forward-sweeping and backward-sweeping. This extremely large hysteresis and nonvolatile behavior strongly suggest that this behavior is

not a simple ECD at EDL. The rapid decrease in i_{ds} at V_{gs} of -1 V (indicated as (c)) indicates conductivity switching between two discrete conductivity states: insulating state and conductive state.

The conductivity modulations in the EDLT are classified into two types. One, indicated as (a) and (c) in Fig. 2, is nonvolatile conductivity modulation, namely five orders, caused by redox reaction between GO and rGO. The other conductivity modulation, indicated as (b) in Fig. 2, is volatile conductivity modulation due to electrostatic modulation of the electronic carrier caused by the EDL at the rGO/YSZ interface. GO shows both *n*- and *p*-type conduction depending on the Fermi level, which can be modulated by using chemical or ECD method.[23] The V_{gs} dependence of i_d in region (b) makes the EDL model with *p*-type conduction a reasonable explanation.

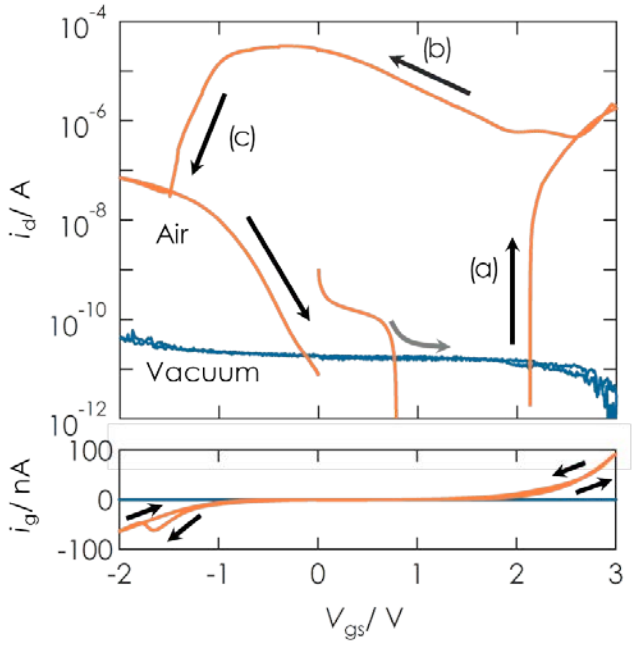

Fig. 2 Electrical transport properties of GO-based EDLT measured in air and vacuum: i_d vs. V_{gs} (upper panel) and i_g vs. V_{gs} (lower panel). V_{ds} was 0.5 V.

UV-Vis-NIR reflectance measurement

UV-Vis-NIR reflectance measurement was used to investigate modulation of the optical property of GO in a two-terminal cell with an ITO electrode/GO/YSZ/Pt multilayer structure. Because detailed information about the band gap cannot be obtained by the form of reflectance (%*R*), the %*R* was converted into Kubelka-Munk (K-M) function ($^{F(R_\infty)}$), which is equivalent to absorbance (α), and then plotted as a Tauc plot in indirect transition. The dc bias dependence of the bandgap energy calculated from the Tauc plot is shown in Fig. 3. As a positive bias was applied, the band gap decreased from V = 2 V and reached 0.30 eV at 5 V. In contrast, the band gap immediately increased when -1 V was applied and saturated at 0.75 eV, which is slightly larger than the initial value of 0.69 eV. This reversible variation of is attributed to bandgap tuning in the GO.

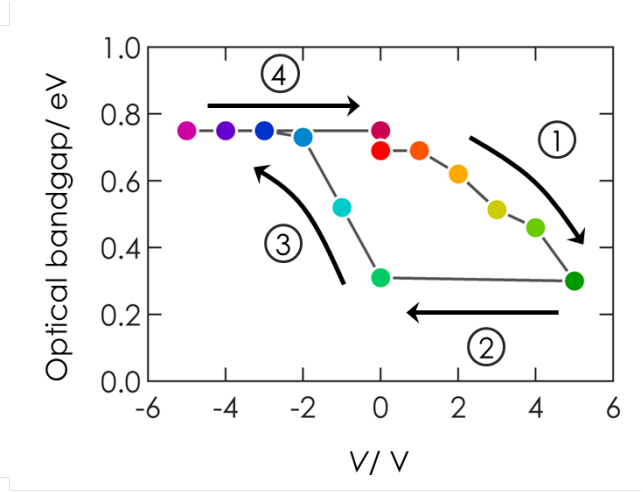

Fig. 3 dc bias dependence of optical band gap measured by UV-Vis-NIR reflectance measurement. Optical band gap is calculated by linear approximation in photon energy range 2.3 to 3.1 eV.

4. Conclusions

An all-solid-state EDLT using GO and YSZ was fabricated based on solid state ionics. The variation in the optical band gap at the GO/YSZ interface was measured by UV-Vis-NIR reflectance spectroscopy and calculated to be from 0.75 to 0.30 eV. It is interesting to note that nanoionic motion of protons at the GO/YSZ interface resulted in both sp^2/sp^3 fraction variation in the GO and high EDL capacity. While the ECD operation response is limited below 10 Hz, potential application of the reversible and in-situ tuning of the sp^2/sp^3 fraction includes not only FETs but also optical, PL, magnetic, and superconducting devices.

References

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