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Short Communication

The effect of oxygen functional groups on the electrical transport behavior of a single piece multi-layered graphene oxide

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ABSTRACT

To investigate the electronic transport mechanisms in multi-layered graphene oxide (MGO), the temperature-dependent electrical conductivity ($\sigma(T)$) has been measured as a function of the annealing temperature (T_a). An individual MGO flake was gradually reduced by thermal annealing at T_a from 88 to 300 °C, with the reduction process confirmed at each stage by X-ray photoelectron spectroscopy. As T_a increases, the $\sigma(T)$ of the MGO also increases. We found that the $\sigma(T)$ is well interpreted by variable-range hopping in disordered regions in series through activated conduction across small barriers. We associate the localized states for hopping with the oxygen functional groups in GO, as well as the small activation barriers with the domain boundaries between the clustered oxygen functional groups and the graphitic region. Both the hopping and activation barrier resistances decrease systematically as the T_a increases.

1. Introduction

Graphene has been researched extensively since it has exotic properties such as the anomalous quantum Hall effect caused by peculiar band structure and excellent electrical, mechanical, thermal, and optical properties [1–5]. However, the electronic structure of graphene must be controlled to apply in the electronics industry. Not only nanosized graphenes such as nano-ribbon [6], nano-flakes [7] and quantum dots but doped graphene [8–11] is considered as the potential components for nanoelectronic devices. Moreover, for a practical application of graphene, the mass production is important as well as electronic modification. Therefore, reduced graphene oxide (GO) has been regarded as a promising material for application.

GO is easily dispersed in water due to the oxygen functional groups (hydroxyl, epoxy, carbonyl, and carboxyl groups) that allow it to easily manipulate the graphene. Multi-layered GO (MGO) is also known to have a layered structure with an interlayer distance that varies from 0.6 to 1.2 nm [12,13]. Due to these properties, GO has been used as a building block for various applications in composites, transparent paper-like materials, mechanical actuators, nanorobots, molecular sensors, supercapacitors, and hydrogen storage materials [14–21]. Intrinsic properties, like the oxygen atom sites in GO and the oxygen concentration-dependence of the conductivity (σ) have been investigated [22–33]. However, there is still an open issue regarding the charge transport mechanisms of GO. Various conduction mechanisms such as Mott variable range hopping (VRH) [26–29], Efros–Shklovskii (ES) VRH (the modified VRH model that considers the Coulomb gap) [30], Arrhenius (activated) behavior [31,32], and fluctuation-induced tunneling (FIT) [33] conduction have been suggested. An Arrhenius (activated) behavior fits well in the high and low temperature regime, but not for the temperature range as a whole [32]. The VRH models, including the ES-VRH mechanism, have been proposed to explain the electrical conduction of reduced GO, because the oxygen functional groups of GO produce localized charge carriers. Both models focus on the oxygen functional groups in order to interpret the conduction mechanism of GO. The theoretical calculations suggested that the oxygen functional groups on the carbon atoms were formed as a clustered structure, much like the clustered hydrogen

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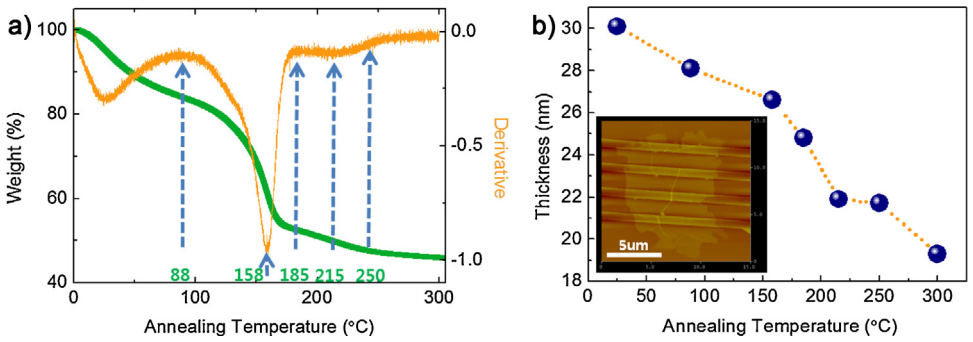

Fig. 1. (a) Thermogravimetric profile of the MGO (Green line). The orange line is the slope of the TGA curve while the blue dotted arrows are the inflection points of TGA. (b) The thickness variation of MGO as a function of T_a obtained from the AFM study. Inset shows the AFM image of the MGO. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

atoms on a carbon surface [34–36]. This indicates that the GO is composed of the carbon domains functionalized by oxygen groups and the graphitic region. The domain is distinguished from the graphitic region by a domain boundary, so the conduction mechanism in MGO can form a combination of two different mechanisms: one from the oxygen functional groups and the other from the domain boundary. Unlike an earlier study [27] that investigated GO films, we report the temperature-dependent conductivity ($\sigma(T)$) of individual MGO flakes subject to different annealing conditions. We show that combining VRH and activated conduction in series is required to understand the overall conduction behavior of the reduced MGO.

2. Experimental

2.1. Device fabrication

GO sheets were produced by utilizing the Hummers method [37] while the GO devices were prepared by drop casting, which is applicable for a wide range of substrates. The GO sheets were obtained via ultra-sonication in deionized water using a bath-type sonicator before the solution was centrifuged at 10,000 rpm for 5 min. Then, the supernatant was dropped onto the highly p-doped ($\rho < 0.005\ \Omega$ cm) silicon wafer covered by a thermally grown SiO_2 layer (300 nm thickness). Before it was fully dried, the dropped solution was blown out with N_2 gas to avoid a densely packed GO layer. A conventional electron-beam lithography (VEGA MM5150 with 30 keV, TESCAN) and Ti/Au (5/50 nm) was deposited on top of the GO using the thermal evaporation system (MHS-1800, Muhan Vacuum) in order to define the electrode.

2.2. Electrical measurement

The devices were placed on a horizontal tube-type furnace (Ajeon Heating Industry) to reduce the GO. Before thermal annealing was conducted, we pumped out the chamber ($<10^{-2}$ Torr) to remove any remaining gas or water in the air. The flow rate of Ar gas was 100 sccm and thermal annealing was performed at 88, 158, 185, 215, 250, and 300 °C for 2 h.

From the thermogravimetric analysis (TGA), we observed GO decreasing in sheet mass. We then selected the annealing temperatures based on the inflection point of the curve in the TGA profile. The tapping mode AFM at 0.5 Hz confirmed the decrease in the GO sheet's height while the annealing temperature increased. XPS was also carried out to probe the components of the GO sheet, and the $\sigma(T)$ was measured using a closed loop cryogenic system with a temperature controller (331 Temperature controller, Lakeshore). The current-voltage characteristics and $\sigma(T)$ vs. gate voltage (V_G) were measured with a semiconductor characterization system (SCS-4200, Keithley) at temperatures from 300 K to 60 K.

3. Results and discussion

3.1. Thermal reduction

The thermal annealing temperature, T_a, of GO was determined using thermogravimetric analysis (TGA) (Fig. 1(a)). We were able to find the GO weight loss in a temperature range from 20 °C to 185 °C, which was possible due to the trapped water evaporation and loosely bound functional groups. Further mass loss was found to occur between 185 °C and 250 °C and was attributed to the removal of tightly bound oxygen functional groups [38]. The TGA profile shows five different inflection points, defined as T_a (T_a = 88, 158, 185, 215, 250, and 300 °C). The thickness of the reduced MGO as a function of T_a was measured through atomic force microscopy (AFM) in Fig. 1(b), which showed that as the T_a increased, the thickness (t) decreased from 30.1 nm (~34 layers of GO) to 19.3 nm.

3.2. XPS spectra

The reduction of the (M)GO was also investigated with XPS (Fig. 2). The sp^2 carbon (C=C), hydroxyl (C—OH), epoxide (C—O—C), carbonyl (C=O), and carboxyl (O=C—O) groups were acted as expected. Before thermal annealing (at room temperature), 45% of the C=C and 40% of the C—O—C species existed. As T_a increased, the amount of C=C species slightly increased but that of C—O—C

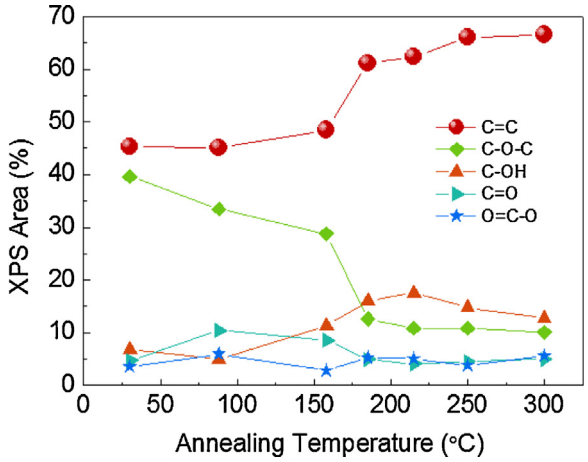

Fig. 2. The variation of the amount of carbon and oxygen groups as T_a increases. The C=C species in MGO was initially 45% and increased to 66% after annealing at 300 °C.