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Structural evolution of graphene in air at the electrical breakdown limit

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ABSTRACT

In application of graphene to real electronics, understanding the mechanism of the electrical breakdown of the graphene in harsh environments should precede many activities in tamed conditions. In this article, we report the unusual structural evolution of microbridge graphene *in air* near the electrical current-breakdown limit. *In-situ* micro-Raman study revealed that Joule heating near the electrical breakdown gave rise to a substantial structural evolution: a previously unknown broad amorphous-like and partially reversible phase at an on- and off-current of ~3.0 × 10^8 A/cm^2, which finally drove the phase to the electrical current-breakdown. Our calculations suggest that the phase originates from the broken symmetry caused by defect formations during Joule heating. In particular, these formations are bonds of carbon-oxygen and vacancies-oxygen. A collection of energetically favorable vacancies-oxygen pairs results in porous graphene, and its evolution can be the key to understanding how the breakdown starts and propagates in graphene under high current density in air.

1. Introduction

Graphene, a single layer of graphite, has many electrical features that are not readily found in other materials, which makes it promising for future electronic devices [1–4]. Though research on graphene-based nanoelectronic applications has been extensive [5–9], the behavior of graphene in harsh environments is still ill understood. In particular, no significant progress has been made under harsh conditions such as under electrical current as high as that at which graphene starts to break down and under ambient conditions. Applications tested so far have not allowed observations at such extremes not only because of their poor design but also because of contamination introduced during fabrication. The breakdown of the graphene/metal contact due to the high contact resistance and stress concentration, for instance, has limited the study of the electrical behavior of graphene to currents far lower than those at which graphene itself reacts to the applied current [10–12]. In addition, most experiments on electrical measurements and surface control has been carried out at low temperature in vacuum, an ideal condition, rather than at room temperature in air. The gas species in air have kept researchers from examining graphene's electrical behavior at its breakdown limit.

Here, we report our observation of the unusual structural evolution of graphene *in air* as we increase current density to ~3.0 × 10^8 A/cm^2, which is near graphene's electrical breakdown limit. To the best of our knowledge, such high current density has never been applied at room temperature under ambient conditions. Our study was made possible by our unique design of microbridge graphene, and our observation of the structural evolution in conjunction with calculation results provides a vital clue to

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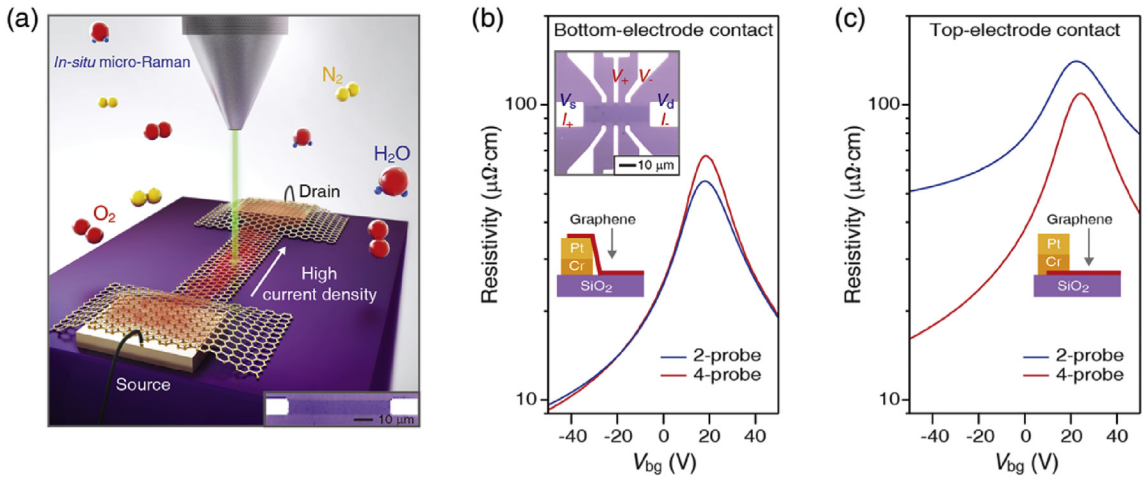

Fig. 1. (a) An illustration of the microbridge of single-layer graphene and *in-situ* micro-Raman measurements under an ambient condition. Change in resistivity as a function of back gate voltage (V_{bg}) in Hall patterns having (b) the bottom-electrode and (c) the top-electrode contact type. (A color version of this figure can be viewed online).

understanding the breakdown mechanism of graphene and carbon-based devices at room temperature under ambient conditions.

2. Experimental

2.1. Sample preparation

Single-layer graphene (SLG) sheets were prepared by chemical vapor deposition (CVD) on Cu foils, and each sheet was transferred onto a heavily p-doped Si substrate with 300 nm-thick SiO_2 on top [13,14]. Microbridge graphene (10 μm × 70 μm) and Hall devices were patterned by electron-beam lithography and O_2 plasma etching.

2.2. Raman spectroscopy and AFM analysis

In-situ micro-Raman measurements were performed on the microbridge graphene in air with electrical current in repeating on and off cycles [15]. Each acquisition time of the Raman measurements was 2 min with an off-current interval of about 2 min between each acquisition. *Ex-situ* micro-Raman scattering spectra were also acquired with the 514.5 nm line of an Ar ion laser as an excitation source (×90 magnification, 0.71 NA) [16]. The spatial resolution of micro-Raman spectroscopy was about 500 nm in diameter. Surface topology was acquired by noncontact mode atomic force microscopy (AFM) with a 45° angle between tip and sample surface using a silicon cantilever controlled by a 100 kHz tuning fork [16].

2.3. Computational simulation

We performed semi-classical molecular dynamics (MD) simulations using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [17], to investigate the structural evolution during oxidation of graphene at 600 K. The simulation temperature was chosen to mimic the Joule heating caused by the application of current densities [5,6,15,18,19]. A reactive force field between oxygen and carbon was applied to determine the chemical reaction between them [20].

3. Results and discussion

3.1. Fabrication of the microbridge graphene and graphene/electrode contact

We were able to fabricate the microbridge graphene out of the large-scale chemical vapor deposited (CVD) graphene [13,14] by simple, one-step electron-beam lithography without additional deposition of a metal electrode as illustrated in Fig. 1a and Fig. S1 (Supplementary Information). This fabrication design allowed us to significantly reduce structural defects of graphene that are introduced by additional fabrication processes and to avoid thermal-stress concentration resulting from a rapid thermal cycle. In this study, we utilize our finding that graphene *on* Cr/Pt (a bottom-electrode contact type, C_B) has a contact resistance significantly smaller than that of graphene *under* Cr/Pt (a top-electrode contact type, C_T), as shown in Fig. 1b and c. In the case of C_B, the resistivity measured with a 2-probe method was close to that measured with a 4-probe method (Fig. 1b), i.e., contact resistance was significantly low in device with C_B. We supposed that low contact resistance in our device was resulted from large difference of workfunction between graphene and Pt electrode, which makes C_B suitable for studying electrical breakdown phenomena because its configuration can reduce the concentration of both Joule heating and thermal stress at the contact under the high current. As a result, our microbridge graphene was able to endure a current density of up to 3.0×10^8 A/cm^2 *in air* before the electrical breakdown occurred.

3.2. In-situ micro-Raman spectroscopy

We carried out *in-situ* micro-Raman spectroscopy on microbridge graphene in air as we applied electrical current in repeating on and off cycles until the graphene reached electrical breakdown. Raman spectra shown in Fig. 2a indicate the dramatic structural deformation of microbridge graphene induced by high current density. Note that the on-current Raman spectra of microbridge graphene experiencing high current density (ranging from 1.3 to 2.6×10^8 A/cm^2) were significantly different from the spectra at off-current. The peaks near the original D and G peaks of pristine graphene became broad and their intensities rapidly grew when the current density exceeded 2.0×10^8 A/cm^2. Graphene oxide also