

論文内容の要旨

論文題目

Fabrication and Characterization of Chemically Synthesized Graphenes

(化学的手法によるグラフェンの合成・修飾とその構造・物性に関する研究)

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Introduction

Graphene is one or a few layer graphite sheet which consists of sp^2 carbon. Since it was isolated in 2004, graphene has been paid much attention due to its peculiar properties such as high mobility as much as $200000\text{cm}^2/\text{V}\cdot\text{s}$, anomalous quantum hall effect at RT and edge state originating from zigzag edge. Moreover, graphene is expected new catalytic material for its high surface area. When we consider its application to devices, however, graphene has several problems to be solved. A new method for high-through put preparation is needed, replacing the present exfoliation method which gives the best quality graphene. CVD growth on metal substrates, thermal annealing of SiC and chemically preparation via graphene oxide (GO) are expected as promising candidates. I have focused on chemical exfoliation of graphene in my thesis. Chemically prepared graphene is suitable for industrial application because it does not need vacuum and high temperature. However, its typical domain size was smaller than $1\mu\text{m}$ and reduction process is necessary to be used as graphene. In my thesis I investigated relationship between conductivity and reduction process, which was not understood in detail. The other problem for graphene is about its electric property. Graphene is originally a zero-gap semiconductor and it causes low on/off ratio of graphene transistor. Thus opening of band-gap is crucial for device application. Theoretically speaking, when nitrogen and boron atom are doped into graphene network, band gap will open. Moreover doping of nitrogen is reported to enhance catalytic properties. However, there have been only a few experimental reports about nitrogen doping to graphene. Therefore in my thesis I examined to apply CVD method to fabricate nitrogen doped graphene (NG) and analyzed NG by scanning tunneling microscopy.

Fabrication and reduction process of graphene oxide

First I examined to synthesize large size GO sheets. GO was prepared by modified Hummers methods. I succeeded in preparing GO on substrate without ultra-sonication which would have made graphene sheet small. I could obtain large size monolayer GO sheets (Fig. 2) easily and repeatedly. I constructed the equipment for in situ conductivity measurement, in which electrical properties could be measured in vacuum during hydrazine (the most powerful reductant for GO) reduction or during thermal annealing. Since the conductivity of graphene is sensitive to adsorbates, in situ conductivity measurement is essential to extract intrinsic properties of graphene oxide. Evolution of conductivity was pursued during two different reduction processes; thermal annealing after or before hydrazine treatment. In the both cases current increased drastically at a specific temperature; 390 K for hydrazine and 465 K for only thermal annealing. In order to clarify the

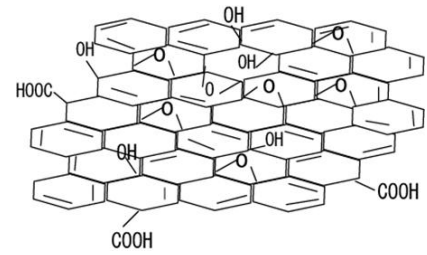


Fig. 1 Graphene Oxide

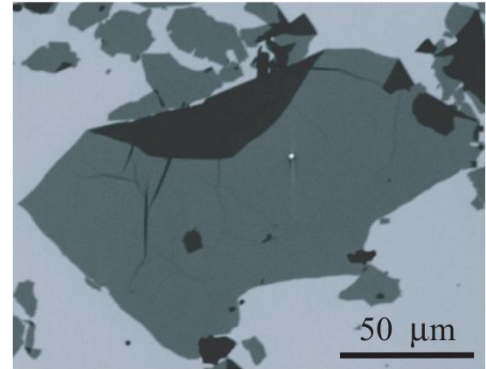


Fig. 2 SEM image of GO

difference of two processes, the transfer characteristic of GO field effect transistor (FET) was investigated and the result is shown in Fig. 3. The specimen reduced by hydrazine after thermal annealing shows lower mobility than the specimen reduced only by hydrazine. In order to elucidate reduction process of GO, XPS spectra were measured during thermal annealing. According to XPS spectra, the peak attributed to C-O bond started to decrease at around 433K and GO was reduced gradually with increasing temperature (Fig. 4). From these results around 465 K the current path was formed by reduction and decrease of C-O bond triggered increase of conductivity. However, the highest mobility of GO FET was $3.0 \text{ cm}^2/\text{V}\cdot\text{s}$ in the present experiment. It is much lower than the exfoliated graphene mainly because GO might have a lot of defects and disorder structure.

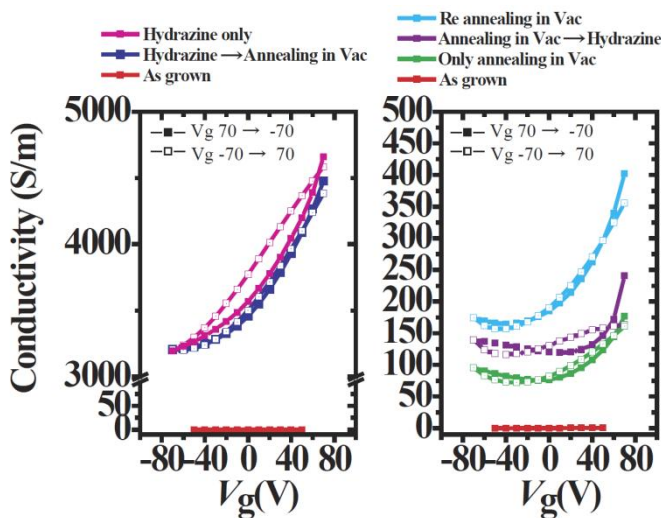


Fig. 3 FET transfer characteristic of each reduction methods

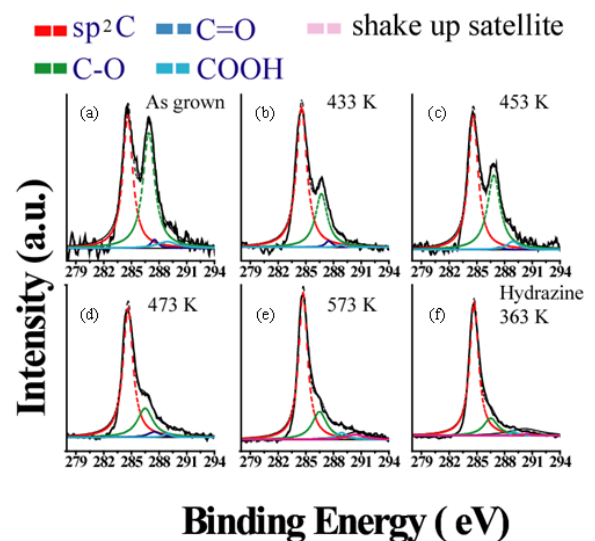


Fig. 4 XPS spectra of C1s during annealing

In order to elucidate atomic structure during reduction process, STM image of GO was observed. The reduced GO (rGO) on Si(100) by thermal annealing at 1300 K showed only a disordered structure and honeycomb lattice intrinsic to graphene could not be found at all. Since graphene is known to grow on several metal substrates by using their catalytic properties, reduction of GO were examined on Pt(111). Fig. 5 indicates an STM image of GO on Pt(111) after thermal annealing at 1300K. Some flat area appeared on GO/Pt(111) and honeycomb lattice could be observed there. This image means that a Pt substrate catalytically restores GO defects and disorder. A moiré structure means monolayer graphene sheet grown on Pt(111).

C 1s XPS spectra of rGO on various substrates were measured (Fig. 6). The FWHM of C1s peak on Pt(111) is as narrow as HOPG, while that on Si(100) is broader reflecting its disorder structure. It can be said that thermal annealing of GO on Pt(111) gives so high quality graphene by utilizing catalytic properties of Pt(111).

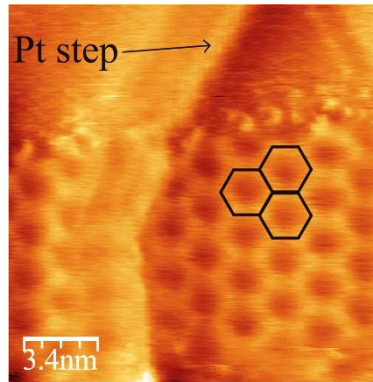


Fig. 5 Moiré structure of GO on Pt(111)
17 nm × 17 nm I_t:5 nA V_s:10 mV

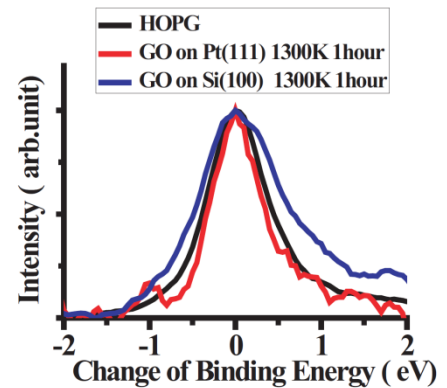


Fig. 6 XPS spectra of C1s

Doping of nitrogen atoms in graphene

Since graphene is known to grow on metal substrates from hydrocarbon (HC) molecules, it can be expected that nitrogen will be doped by using HC molecules which contain nitrogen atoms. First, Pt(111) surface was exposed to 200L(1L = 1.3×10^{-4} Pa/sec) of pyridine at various substrate temperatures. At 850 K a lot of a few nm size domed-shaped structures appeared. Some domains have a honeycomb structure for graphene formed at 1000 K, while domed-shaped domains coexisted. Fig. 7 indicates an STM image of graphene after CVD at 1150 K. A lot of large domains with honeycomb lattice grew on Pt(111) and some moiré patterns also appeared. In some atomic resolution STM images of graphene, a few atoms seem brighter than other atoms and the brighter area is over a few honeycomb rings. (Fig. 8) Nitrogen atom is expected to induce change of electronic state at surrounding carbon atoms in a honeycomb lattice. Therefore existence of bright area images suggests nitrogen atom(s) incorporated into graphene network.

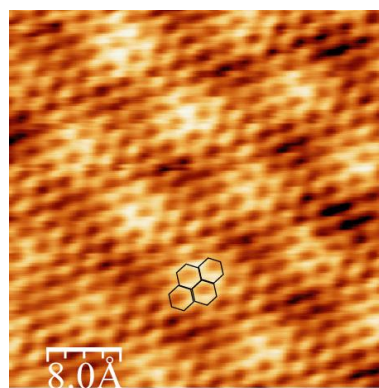


Fig. 7 Moiré and honeycomb Structure of NG on Pt(111)
4 nm × 4 nm I_t:7 nA V_s:10,13 mV

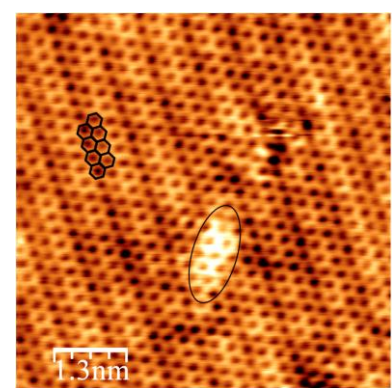


Fig. 8 Bright area in honeycomb lattice
6.313 nm × 6.313 nm I_t:7 nA V_s:-10 mV

Next, adsorption process of oxygen on nitrogen doped graphene was investigated. Fig. 9 shows STM image at the same position before and after exposure to 10L O₂ at RT. Comparing with two images, around defects become brighter. Moreover according to other STM images oxygen also adsorbed at domain boundaries preferably. XPS and STM measurement suggests that doped nitrogen atoms tend to exist at pyridinic sites (around at defects and domain boundary). Thus it can be considered that the nitrogen atoms around defects and domain boundary adsorb oxygen preferentially. The exposure to 600L O₂ at 680 K results in much oxygen adsorption at domain boundary and enhanced modulation amplitude (Fig. 10).

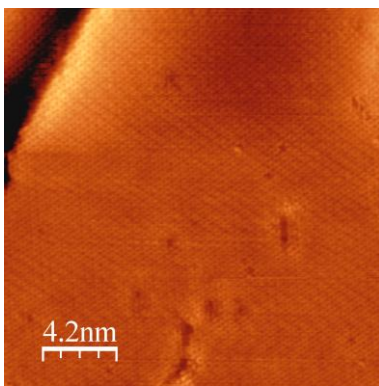


Fig. 9 (a) Before O₂ exposure at RT
NG was prepared by 1150 K exposure
20.8 nm × 20.8 nm I_t: 1 nA V_s: 0.003 V

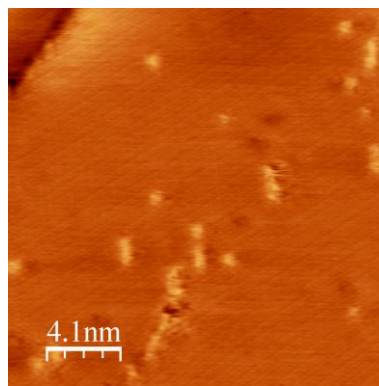


Fig. 9 (b) After O₂ exposure at RT
20.55 nm × 20.55 nm I_t: 1 nA V_s: 0.003 V

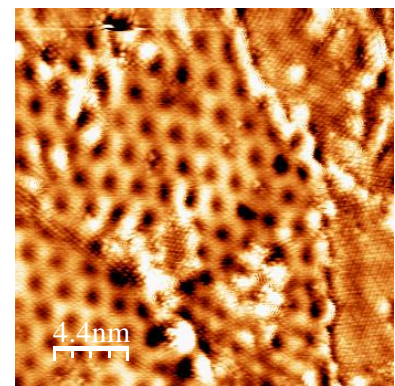


Fig. 10 After O₂ exposure at 680K
NG was prepared by annealing at 1150 K
after 200 L pyridine exposure at RT
22.16 nm × 22.16 nm I_t: 1 nA V_s: 10 mV

Conclusion

I have investigated chemically modified graphene such as graphene oxide and nitrogen doped graphene. I elucidated relationship between composition and electric conductivity of GO in detail and found that thermal reduction method generates a lot of defects in graphene. Moreover, I proved that annealing of GO on Pt(111) at 1300 K provides a graphene without defects and disorder due to catalytic property of Pt. It is a new method for obtaining a high quality graphene from GO. I succeeded in synthesizing a nitrogen doped graphene on Pt(111) from pyridine and investigated atomic structure with STM. Brighter areas in honeycomb lattice indicated nitrogen doping into carbon network. In addition I also investigated oxygen adsorption on a nitrogen doped graphene. Oxygen tends to be adsorbed around defects and domain boundary of graphene where nitrogen atoms may exist selectively. The change of moiré pattern by oxygen indicates adsorption was affected by moiré pattern, corresponding to modulation of electronic state caused by interaction with Pt(111) substrate.