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# RF plasma Assisted Nitrogen Doping to Graphene Lattice
# RFプラズマを用いたグラフェン格子への窒素ドープ

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Nitrogen doping is expected to provide several intriguing properties to graphene. Nitrogen plasma treatment to highly oriented pyrolytic graphite (HOPG) and graphene oxide (GO) samples causes doping of nitrogen atom into the graphene layer. The amount and the site of doped nitrogen atoms depend on the plasma treatment time and the initial state of material. The nitrogen doping changes the work function of graphene layer from 4.3 eV to 5.4 eV and the decreases the band gap of GO. The plasma treatment is found to be a powerful tool to tailor the electronic states of graphene-based materials.

## 1. Introduction

Doping of heteroatoms is one of the most promising ways to tune the electronic properties of graphene for achieving various industrial applications. Nitrogen (N)-doped graphene has been investigated as the potential candidates of cathode catalyst for fuel cells, anode materials of lithium-ion batteries, electrodes of bio-sensors, and ultracapacitors, etc. In most of these studies N-doped graphene has been synthesized by a variety of methods and the effect of N content and doped site on the device performance has been clarified. However, the origin of improvement has not been well understood, especially on the basis of electronic structures. In the present work, we have synthesized nitrogen-doped graphene and investigated the effect of nitrogen doping on the electronic structure of graphene.

## 2. Experimental

Synthesis of N-doped graphene has been carried out mostly by direct growth or post treatment. In the present work we exposed a highly oriented pyrolytic graphite (HOPG) substrate and a graphene oxide (GO) sheet to radio frequency (RF) nitrogen plasma. The plasma treatment has several advantages as compared with conventional chemical treatment: usability of safer gases, decrease in substrate temperature, etc. In the experiment the RF power was set at 0.1 W under the working pressure of 0.1 Pa. The specimen was not heated during plasma treatment.

## 3. Result and Discussion

3.1 *Effect of nitrogen doping on the work function of graphene* [1]

We have prepared two kinds of substrates: one was pristine HOPG (p-HOPG) with large grains and the other was damaged HOPG (d-HOPG) which had been exposed to Ar plasma beforehand. Nitrogen doping was carried out to both p-HOPG and d-HOPG. There are several kinds of doped sites as shown in Fig. 1. The nitrogen content

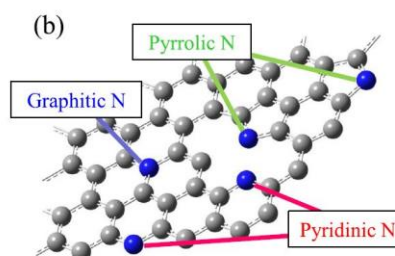


Fig. 1 Nitrogen doped sites in graphene.

with its chemical state was investigated by X-ray photoelectron spectroscopy (XPS). Figure 2 shows the nitrogen content at each doped site as a function of $N_2$ plasma treatment time. In the case of p-HOPG, nitrogen atoms are doped mostly at the graphitic site at the initial stage. As the plasma treatment proceeds, the relative content of

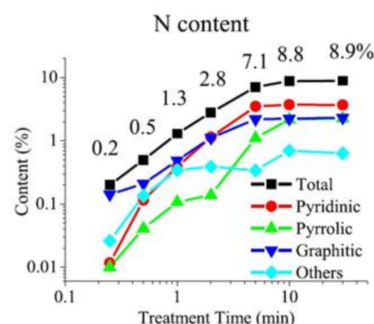


Fig. 2 Nitrogen content at each doped-site as a function of $N_2$ plasma treatment time for p-HOPG. The figures denote total amount of nitrogen content.

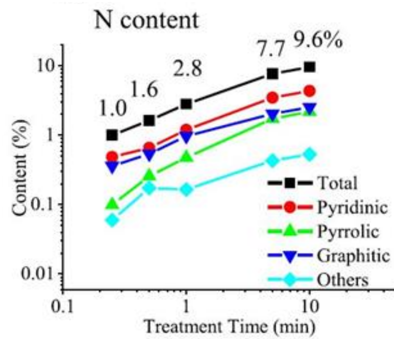


Fig. 3 Nitrogen content at each doped-site as a function of $N_2$ plasma treatment time for d-HOPG. The figures denote the total amount of nitrogen.

pyridinic site increases. After 10 min treatment the nitrogen content is almost saturated and the pyridinic N has the largest content. In the case of d-HOPG, however, the pyridinic N is the main component from the initial stage as shown in Fig.3. This difference is ascribed to the structure, to which the nitrogen atom is incorporated. For the nearly perfect lattice (p-HOPG) only way to dope N is to substitute the constituent C atoms. On the other hand, there exists a considerable amount of edge of graphene lattice in d-HOPG. In that case N atoms has a chance to replace the edge C atoms, resulting in doping at a pyridinic or pyrrolic site.

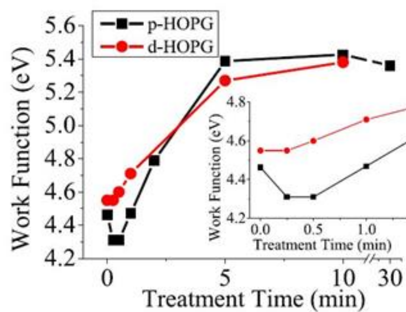


Fig. 4 Change of work function with $N_2$ plasma treatment time for p-HOPG and d-HOPG.

Figure 4 shows the change in work function with increasing $N_2$ plasma treatment time. The work function monotonously increases with nitrogen doping for d-HOPG, while it firstly decreases and re-increases for p-HOPG. The difference reflects the fact that graphitic or pyridinic nitrogen decreases or increases the work function.

3.2 *Effect of nitrogen doping on the band gap of GO*

GO is a semiconductor or an insulator with a band gap larger than 2 eV [2]. RF plasma treatment to GO causes not only nitrogen doping but also reduction. The oxygen content decreases with treatment time together with an increase of nitrogen content. The feature of doping resembles that of d-HOPG in a way that nitrogen atoms are doped at a pyridinic or pyrrolic site from the initial stage. Figure 5 shows the change of valence electronic states of GO with $N_2$ plasma treatment. As-grown GO has a wide gap below the Fermi level (0 eV). With increasing plasma treatment time the valence band maximum becomes shallower. Since the conduction minimum is not known at the present stage, the decrease of band gap is 1.1 eV at least. In the case of chemical treatment by use of hydrazine, it takes several tens of hours to reduce the band gap by 1 eV [3]. The present plasma treatment is found to be effective for reduction of GO.

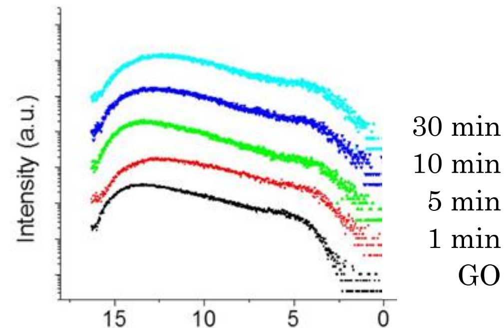


Fig. 5 Change of valence band electronic states of GO with $N_2$ plasma treatment.

## 4. Summary

Use of RF plasma is a promising way to tune the electronic property of graphene-based materials. We show the examples to control the work function of HOPG and the band gap of GO.

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**References**

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