

# Bias Dependent G-band Shift of Graphene in Direct Contact with Ni

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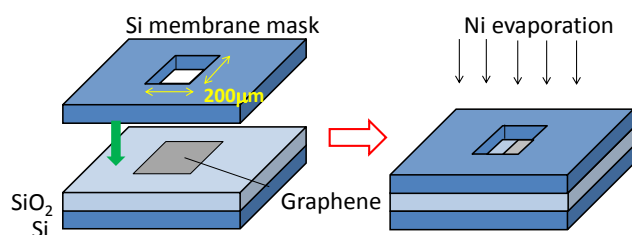
## 1. Introduction

We have so far paid attention to the graphene/metal contact properties since the contact resistance is expected to be the most critical obstacle for miniaturization of the device [1]. Recently, using the multi-terminal device fabricated by EB lithography technique with the PMMA resist, we have demonstrated that the carrier density in graphene underneath Ni electrode is modulated [2]. This new finding is expected to be the key to reduce the contact resistance, since it is possible to increase the density of states of graphene underneath the metal electrode by an additional buried electrode.

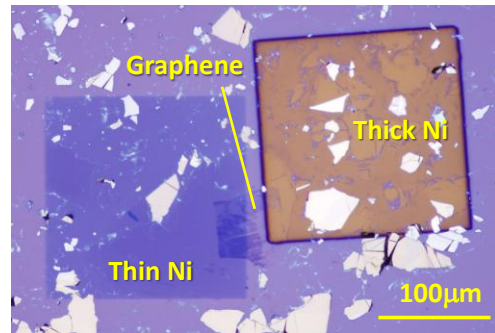
However, the existence of the firmly attached PMMA resist residual on graphene is known even after its removal by hot acetone from the early stage of graphene research [3]. Therefore, it is not clear whether the carrier density modulation in graphene underneath the metal electrode is intrinsic characteristics or not, as far as the resist material is utilized in the device fabrication process. In this research, we established resist-free metal deposition technique and then investigated it by Raman G-band modulation.

## 2. Device Fabrication

As the substrate,  $n^+$ -Si with 90-nm thick  $\text{SiO}_2$  was used. Before the graphene transfer,  $\text{SiO}_2$  surface was subjected to  $\text{Ar}/\text{O}_2$  plasma treatment in order to obtain large graphene [4]. Then, graphene was transferred onto the substrate by the mechanical exfoliation of Kish graphite. The layer number was confirmed by the optical



**Fig. 1.** Schematic illustration of resist-free process using Si membrane mask.

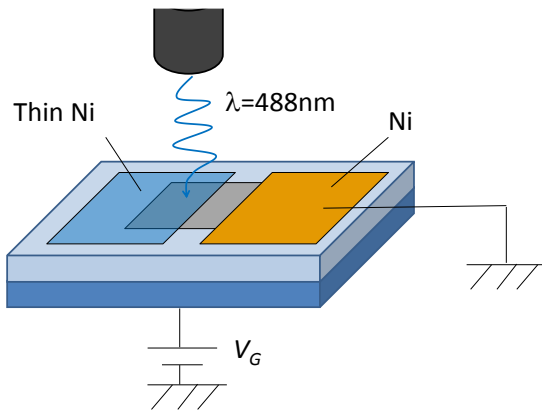


**Fig. 2.** Optical micrograph of the graphene device fabricated by resist-free process.

contrast and Raman microscopy. The Si membrane mask with  $200\ \mu\text{m} \times 200\ \mu\text{m}$  square window was used to fabricate the metal electrode by resist-free process, as shown in **Fig. 1**. Thin ( $\sim 2\ \text{nm}$ ) and thick Ni ( $\sim 10\ \text{nm}$ ) were deposited on the both side of graphene by thermal evaporation. To avoid the contamination at the graphene/Ni interface, the process from graphene transfer to Ni deposition was conducted rapidly. **Figure 2** shows an optical micrograph of the fabricated graphene device.

## 3. Measurement Method

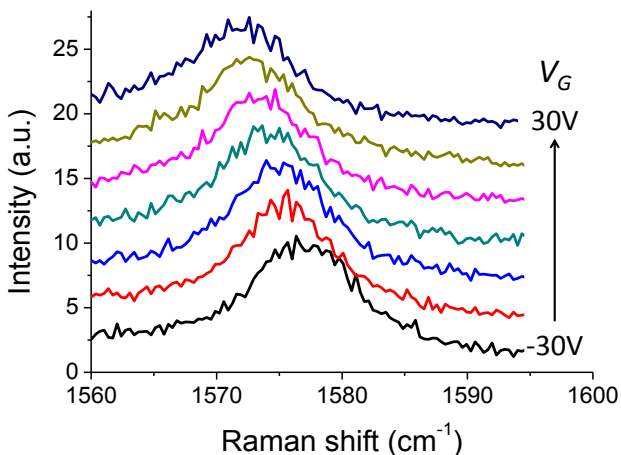
For the detection of gate modulation of graphene under the Ni electrode, microscopic Raman spectroscopy measurements were carried out by Ar laser with  $\lambda = 488\ \text{nm}$  and a power of 0.5 mW just below the objective lens. It is well known that the Raman G band ( $\sim 1600\ \text{cm}^{-1}$ ) is modulated by the back gate voltage due to the release from the electron-phonon coupling ascribed to Kohn anomalies at  $\Gamma$  point [5]. **Figure 3** shows the schematic illustration of the experimental setup. The thick Ni electrode was connected to the ground and Raman spectra were measured through the thin Ni film with changing the back-gate voltage ( $V_G$ ). The acquisition time for 1 spectrum was 50 s. In order to avoid the local heating due to the laser, the measurement was conducted under the  $\text{N}_2$  gas flow.



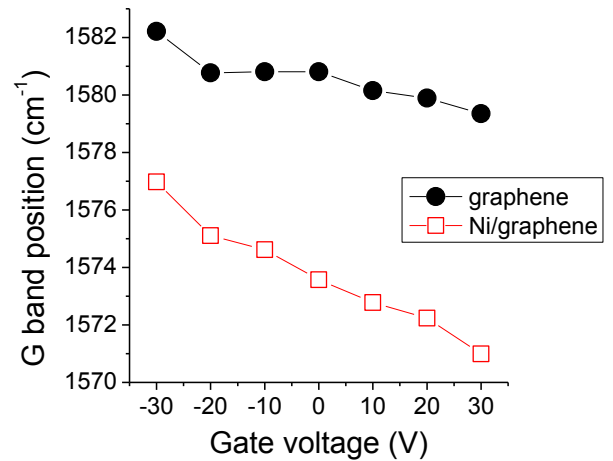
**Fig. 3.** Schematic illustration of Raman measurement under the back-gate bias.

#### 4. Results and Discussion

**Figure 4** shows the Raman G band spectra of graphene underneath the Ni thin film for different  $V_G$ . Although S/N ratio is not so high due to the detection through Ni thin film, clear peak shift was observed as a function of  $V_G$ . **Figure 5** plots peak positions of the G band as a function of  $V_G$  for bare graphene and graphene under Ni thin film. The G band position shifts to lower frequency monotonically with applying positive  $V_G$ . Dirac points of these graphene samples were not observed and should be over 30V. This behavior is consistent with the previous IV measurement where Dirac point was drastically shifted to the positive voltage due to the doping from  $O_2$ -plasma treated  $SiO_2$  surface [4]. Although the qualitative comparison for the amount of G band shift is difficult at present, the G band shift of graphene underneath Ni thin film shows the very similar trend compared with bare graphene case. This result



**Fig. 4.** Raman G band spectra of graphene underneath the Ni thin film for different  $V_G$  ranging from -30V to 30V (10V step).



**Fig. 5.** Peak positions of the G band as a function of  $V_G$  for bare graphene and graphene under Ni thin film.

reveals that carrier density modulation in graphene indeed occurs even at the graphene/Ni contact without resist residue.

#### Conclusions

We have developed the resist-free metal deposition technique using Si MEMS mask. Based on the similar Raman G band shift, it can be concluded that the carrier density in graphene underneath the Ni electrode is modulated.

#### Acknowledgement

We are grateful to Dr. E. Toya in Covalent Materials for kindly providing us Kish graphite. This work was partly supported by the Japan Society for the Promotion of Science (JSPS) through its "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)".

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