Research Paper

Study of a Radical Doping Method for Large-area Two-dimensional Materials

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Abstract

Graphene has been studied owing its interesting properties. In particular, several studies have been conducted to replace transparent electrodes such as indium tin oxide. However, replacing graphene with transparent electrodes has been difficult due to problems such as high sheet resistance. In this study, we investigated a doping method using radicals with a mesh grid module in plasma to overcome this problem. With the proposed method, severe physical damage to graphene was not observed through Raman spectroscopy, and graphene films with a 52 % reduction rate in sheet resistance after doping were produced. Additionally, the reduction non-uniformity was determined using a 6-inch wafer and was found to be only ~2.25 %.

Keywords: Graphene, Doping, Radical, Sheet resistance

I. Introduction

Graphene has been widely investigated owing to its unique properties such as its mechanical flexibility, high optical transparency, and low electrical resistivity [1-9]. In particular, graphene has been attracting much interest as an alternative to indium tin oxide (ITO), a transparent electrode material used in solar cells and touch screens, because of its very high carrier mobility, high transparency, and excellent flexibility [9-15]. Toward this, various studies have been carried out and progress has been made in the synthesis of large-area graphene through chemical vapor deposition (CVD) techniques. However, graphene synthesized by CVD has issues such as high sheet resistance compared to that of ideal graphene, owing to defects such as domains, grain boundaries, and wrinkles, and the synthetic processes are not easily scalable [9-12,14-16]. Because of these drawbacks, attempts have been made to improve the sheet resistance through various doping methods, including chemical, plasma, metal, and photochemical methods. However, although these doping methods effectively reduce the transmittance, graphene suffers damage due to energetic ions in the plasma, undergoes agglomeration due to metal particles, and

the graphene conducting system is broken by photochemical methods [11-13,17-20].

In this study, we propose a controllable radical doping method using a mesh grid module to realize a graphene film with low sheet resistance, while maintaining the nature of graphene. To realize a doping method that is controllable and does not destroy the graphene network, a mesh grid module was inserted into the process chamber to remove energetic ions. Using the proposed method, we produced graphene films with 52 % reduction rate of the sheet resistance after doping, without damaging the graphene structure. Moreover, the non-uniformity of the reduction in the sheet resistance was determined using a 6-inch wafer and non-uniformity of only ~2.25 % was observed.

II. Experimental details

A. Radical doping system

As shown in Fig. 1, experiments were carried out using an inductively couple plasma (ICP) system with an internal-type linear antenna. The ICP source was composed of a 6-mm-diameter copper tube and the outer surface of the copper tube was coaxially covered with a quartz tube of 10 mm diameter and 2 mm thickness. A 13.56 MHz radio frequency (RF) power source was connected to the internal ICP source through an

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Figure 1. (Color online) Schematic diagram of radical doping system with a mesh grid module.

L-type matching network, and the power was varied from 10 to 50 W at 10 mTorr under 100 sccm of Cl_2 gas. The inner diameter of the process chamber was 32 cm and the substrate diameter was 16 cm. The substrate could be inserted into the process chamber using a load lock system without breaking the vacuum. To generate plasma for doping, Cl_2 gas was used and a double mesh grid module was inserted to block most of energetic ions in the plasma. A retarding field analyzer (RFA, SEMION from Impedance Inc.) was located on the substrate to examine the presence and energy distribution of ions that could damage graphene.

B. Synthesis and transfer of graphene

A copper foil with $100 \times 90 \text{ cm}^2$ area (99.99 %, 75 μm thickness) was placed in a vacuum-pumped tube furnace and the temperature of the furnace was increased up to 1050 $^\circ\text{C}$ under 10 sccm H_2 for 1 h. After annealing at this temperature prior to growth, graphene was synthesized at 1050 $^\circ\text{C}$ for 30 min using H_2 (10 sccm)/ CH_4 (20 sccm), and then the tube was cooled to room temperature. The as-grown graphene was coated with poly(methyl methacrylate) (PMMA), and immersed in a copper etchant (FeCl_3) solution to etch away the copper foil. After that, the PMMA-coated graphene was transferred onto a SiO_2 substrate and PMMA was dissolved in acetone.

C. Characterization

Changes in the sheet resistance of the graphene film on SiO_2 according to the doping level were determined with a sheet resistance meter (FPP-2400, Dasoleng Inc.), and graphene having a sheet resistance of 680–710 ohm/sq. was used for doping process. To understand the effect of doping, Raman spectral analysis

was carried out. Raman spectroscopy (RM-1000, Renishaw) was performed with a laser wavelength of 514 nm.

III. Results and discussion

Figure 2 shows the ion energy distribution of ions incident on the substrate with and without the mesh grid, according to the change in the input power and process pressure, which was determined using an ion energy analyzer. The top and middle plots in Fig. 2(a) show the results of measuring the ion energy incident on the substrate with an increase in the input power from 100 to 200 W, under the process pressure conditions of 10 mTorr of Ar. As shown, the energy of the ions reaching the substrate increases as the input power increases. However, when a mesh grid is inserted, energetic ions could not be observed under any input power condition. The top and middle plots in Fig. 2(b) show changes in the energy of the ions incident on the substrate with an increase in the process pressure from 5 to 10 mTorr. As the process pressure increases, the energy of the ions incident on the substrate is observed to move toward a lower energy; however, when the mesh grid is inserted, no ions can be observed. The results suggest that the mesh grid module efficiently removes the energetic ions and electrons in the plasma and selectively extracts low-energy chlorine radicals.

To investigate the structural damage to graphene during the plasma-doping process, the Raman spectrum of graphene exposed to Cl_2 plasma was analyzed in comparison with that of graphene not exposed to Cl_2 plasma. In general, if the graphene structure is damaged, the D peak (located near 1350 cm^{-1}) emerges

Figure 2. (Color online) The measured ion energy distribution incident on the substrate with and without the mesh grid according to the change of (a) input power and (b) process pressure.

Figure 3. (Color online) Raman spectrum for mono-layer graphene before and after the chlorine doping using radical. The chlorine radical was generated using mesh grid at 20 W of RF power with 100 sccm 10mTorr Cl₂.

and the intensity of the 2D peak decreases. As shown in Fig. 3, no severe change in the D peak intensity is observed between pristine and doped graphene samples.

Figure 4. (a) Change in the sheet resistance and (b) I_D/I_G ratio determined from the Raman spectrum with a change in the input power from 10 to 50 W under 10 mTorr of Cl₂ for an exposure time of 15 s.

The G and 2D peak positions of doped graphene, however, are blue-shifted by 5 and 7 cm⁻¹, respectively, implying that the doping polarity is p-type. When a Cl radical reaches the graphene surface, because of the strong electronegativity of the Cl atom, an electron is transferred from the graphene surface to the adsorbed Cl atom. This results in ionic bonding between graphene and Cl atom, without the breakage of the graphene structure. In the case of doping without the mesh grid, the I_D/I_G increased when 20 W RF power was used (not shown). The results of the Raman spectral analysis indicate that the radical doping method using the mesh grid module can change the surface properties of graphene without damaging its structure.

Figure 4 shows the change in the sheet resistance and the I_D/I_G ratio determined from the Raman spectrum with a change in the input power from 10 to 50 W under 10 mTorr of Cl₂ for an exposure time of 15 s. As shown in Fig. 4(a), as the input power increases,

Figure 5. (a) The reduction in the sheet resistance and (b) the I_D/I_G ratio according to the exposure time under 10 mTorr of Cl_2 at 20 W input power.

the reduction rate of the sheet resistance changes from 18 to 40 %, and a reduction rate of the sheet resistance of 40 % is obtained at 20 W input power. Figure 4(b) shows that the I_D/I_G ratio determined from the Raman spectrum does not change significantly with increasing input power. It is considered that most of the energetic ions in the plasma are removed by the mesh grid module and the reactive and high-energy radicals are selectively extracted and used in the doping process.

Figure 5 shows the reduction in the sheet resistance and the I_D/I_G ratio according to the exposure time under 10 mTorr of Cl_2 at 20 W input power. Figure 5(a) shows the reduction in the sheet resistance with a variation in the doping time from 2 to 15 s, and the highest reduction in the sheet resistance of 52 % is observed at 5 s. As shown in Fig. 5(b), the I_D/I_G ratio increases slightly from 5 s as the exposure time increases, but no severe change is observed. This is probably due to the infiltration of a very small amount of ions through the mesh grid module that

Figure 6. (Color online) The sheet resistance of doped graphene placed at seven different positions on a 6-inch wafer

was not detected by the ion energy analyzer, which can be solved by optimizing the grid hole size and interspacing.

In order to confirm the possibility of radical doping on a larger area, Fig. 6 shows the sheet resistance of doped graphene placed at seven different positions on a 6-inch wafer in comparison with that of pristine graphene, as shown in the inset of Fig. 6.

Doping was carried out for 5 s at 20 W input power under 10 mTorr of Cl_2 , and the sheet resistance was measured. As shown in Fig. 6, the reduction rate of the sheet resistance was calculated to be ~43.6 to 45.5 %, with the non-uniformity of the reduction rate being ~2.25 % for a 6-inch wafer.

IV. Conclusions

In this study, through radical doping using a mesh grid module, severe physical damage to graphene was prevented with no significant increase in the I_D/I_G ratio derived from Raman spectroscopy, according to the inductive power and exposed time. Blue shift of the G peak and 2D peak indicating p-type doping was observed and the decrease in the sheet resistance of ~52 % could be achieved. To investigate the possibility of extending the method for large-area graphene doping, non-uniformity of the sheet resistance reduction was determined using a 6-inch wafer and non-uniformity of ~2.25 % was observed.

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