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Plasma treatments to improve metal contacts in graphene field effect transistor

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Graphene formed via chemical vapor deposition was exposed to various plasmas (Ar, O₂, N₂, and H₂) in order to examine its effects on the bonding properties of graphene to metal. After exposing patterned graphene to Ar plasma, the subsequently deposited metal electrodes remained intact, enabling the successful fabrication of field effect transistor arrays. The effects of the enhanced adhesion between graphene and metals were more evident from the O₂ plasma than the Ar, N₂, and H₂ plasmas, suggesting that a chemical reaction of O radicals imparts hydrophilic properties to graphene more effectively than the chemical reaction of H and N radicals or the physical bombardment of Ar ions. The electrical measurements (drain current versus gate voltage) of the field effect transistors before and after Ar plasma exposure confirmed that the plasma treatment is quite effective in controlling the graphene to metal bonding accurately without the need for buffer layers. © 2011 American Institute of Physics. [doi:10.1063/1.3646506]

I. INTRODUCTION

Graphene has attracted worldwide attention as the next generation semiconductor material for replacing silicon because of its unique electrical and physical properties.^{1–3} In particular, extensive research into a range of device applications, such as ultrafast photo-detectors, field effect transistors (FETs), RF devices, and spintronics,^{4–7} has been conducted on account of the extremely high mobility, linear band structure, and controllable band-gap. Recently, large scale graphene was synthesized via chemical vapor deposition (CVD).^{8,9} Nevertheless, it is difficult to deposit electrodes directly onto graphene because of the low interaction energy between the metal and carbon atoms.¹⁰ In order to resolve these problems, the insertion of buffer layers that have a higher interaction energy with graphene (e.g., Ti, Cr) or selective etching have been employed. However, these methods have been found to bring the same issue of the weak interaction with electrodes of the fine patterns under several μm .¹¹ Furthermore these additional processes can increase the cost and also pose problems induced by a transition of the material properties of graphene.

Recently, graphene was known to transform from hydrophobic into hydrophilic by plasma treatments.¹¹ The authors suggested that the adhesion of metal-electrodes can be improved by plasma treatments. According to the Raman spectrum, it appears to be difficult to use plasma-treated graphene for device applications because the intensity of the D peak indicates an unacceptably high defect concentration. Although the Raman results of plasma treated graphene showed properties similar to those of pristine graphene under the weakest plasma power (2 W), there is no clear evidence or mechanism for improving the interaction energy between graphene and electrodes. Liang *et al.* reported that the

adhesion between graphene and electrodes can be improved by O₂ plasma, but the current level and hole mobility of graphene FETs fabricated by the plasma treatment were approximately three times smaller than those without the plasma treatment.¹² In this study, the source and drain regions in the FETs were patterned by a photoresist (PR) and exposed to a range of plasmas in order to improve the bonding of graphene to the electrodes. We showed the pristine-graphene level electrical performance of the plasma treated FETs was examined.

II. EXPERIMENTAL PROCESS

A. Graphene growth

Graphene films were formed via CVD. Thin copper foils were loaded in a vacuum-furnace at temperatures $>1000^\circ\text{C}$. After reaching 10^{-3} Torr, the temperature was increased to 1000°C and maintained for 15 min under a H₂ gas atmosphere. CH₄ and H₂ gas with a 5 to 1 ratio were flowed for 30 min. The graphene films were formed on the copper foils when the foils were cooled rapidly in the same atmosphere. In order to preserve the graphene films during the transfer process, one side of the copper foils was spin-coated using a PMMA solution, and the other side was etched with an inductively coupled plasma etcher using O₂ plasma (gas flow: 30 SCCM [SCCM denotes cubic centimeters per minute at standard temperature and pressure]; power: 60 W; time: 4 s). The PMMA/graphene/copper films were treated with an ammonium persulfate solution (0.05 g/ml) for approximately one day to remove the copper films. After removal, the PMMA/graphene films were transferred to the SiO₂/Si substrates and annealed at 200°C to remove the water molecules, which can impede the adhesion between graphene and the substrates. The PMMA was then dissolved by acetone, and plasma-treatment for device fabrication followed.

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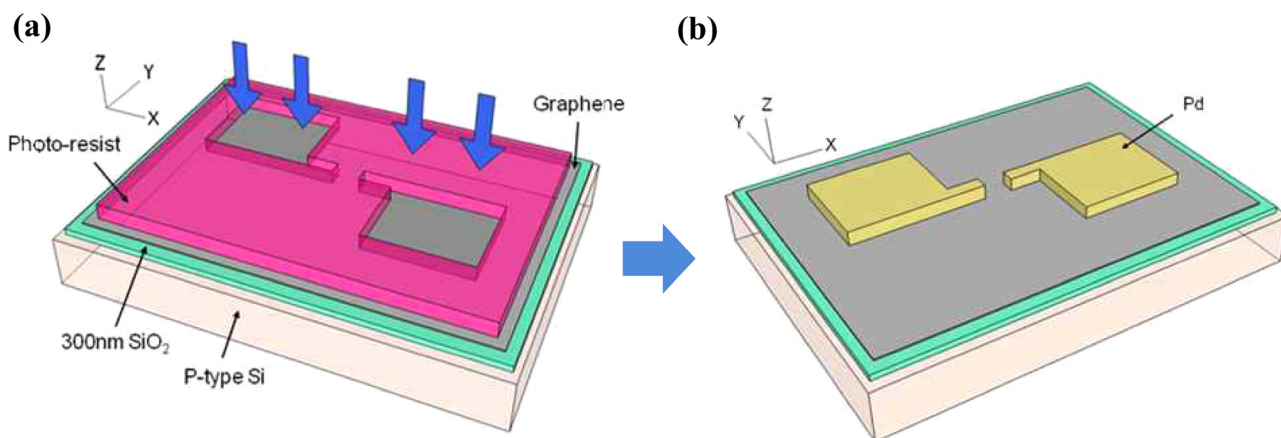


FIG. 1. (Color online) Schematic diagram of the fabrication of graphene FET devices. (a) Graphene was transferred to a 300 nm SiO₂/Si substrate. The graphene patterned by photolithography was exposed to Ar plasma. (b) 50 nm Pd electrodes were deposited on both the plasma treated graphene and PR via e-beam evaporation, and the PR was removed by acetone.

B. Plasma treatment

The following conditions for the plasma discharge were applied in order to improve the adhesion between graphene and metals. To avoid etching or damage to the graphene, low density plasma was produced by applying only dc bias power of 20 W. The Ar flow rate was 30 SCCM, and the working pressure of the chamber was 15 mTorr. Under these conditions, graphene was exposed to plasma for durations of 1, 2, 3, or 4 s. Various gases (H₂, N₂, Ar, and O₂) were used to test the chemical and physical effects of the plasma on graphene surfaces. After the plasma treatment, a transition of the graphene surface was observed based on contact angle measurements, Raman spectroscopy, and Fourier-transformed infrared spectroscopy (FT-IR), which were used to determine the wettability, transition of the bonds and defects, and functional groups, respectively.

C. Device fabrication

Back-gating graphene FETs were fabricated in order to examine the electrical properties of graphene. Figure 1 shows a schematic diagram of the fabrication process for the devices. Graphene formed via CVD was transferred to 300 nm thick SiO₂ grown on a Si substrate. Prior to the plasma treatment, the source and drain regions in the FETs were patterned by photolithography. After exposure to the plasma, Pd electrodes (50 nm) were deposited via electron-

beam evaporation, and the PR was removed by acetone. Using the plasma treatment, approximately 250 FET arrays were fabricated on a substrate (0.8 cm × 0.8 cm). The electrical properties of these devices were measured using a semiconductor analyzer (Agilent 4155 C) at room temperature and under ambient conditions. Furthermore, the yield of the intact electrodes was measured before and after the plasma treatment in order to confirm the improvement in adhesion between graphene and the electrodes.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the Raman spectra of the Ar plasma treated samples for various durations. For pristine graphene, the intensity of the 2D peak was larger than that of the G peak, which indicates monolayer graphene. After the plasma treatment, there was a decrease in the 2D peak, indicating sp² bonding, as well as an increase in the D peak, indicating defects and the breakage of sp² symmetry, which is a relative measure of the amount of sp³ bonding. The S3 peaks near 2950 cm⁻¹ were assigned to a combination of G and D peaks as a result of lattice disorder.¹³ The G peak can be classified into two different peaks, G and D', after the plasma treatment. The D and D' peaks originate from the disorder-induced double resonance Raman scattering process at the edge or defect regions.¹⁴ The generation of D' peaks at 1610 cm⁻¹ indicates that vacancies might be formed by ion bombardment from the

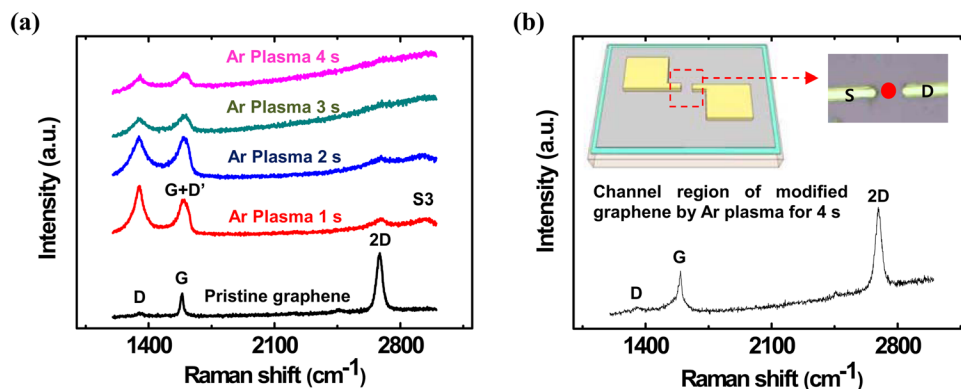


FIG. 2. (Color online) Raman spectra of (a) pristine and Ar plasma treated graphenes and (b) the channel region after Ar plasma treatment for 4 s. The pristine graphene shows a propensity to form a monolayer. After the plasma treatment, Raman spectra of graphene were similar to those of graphene oxide, but the graphene between the source and drain electrodes remained pristine.

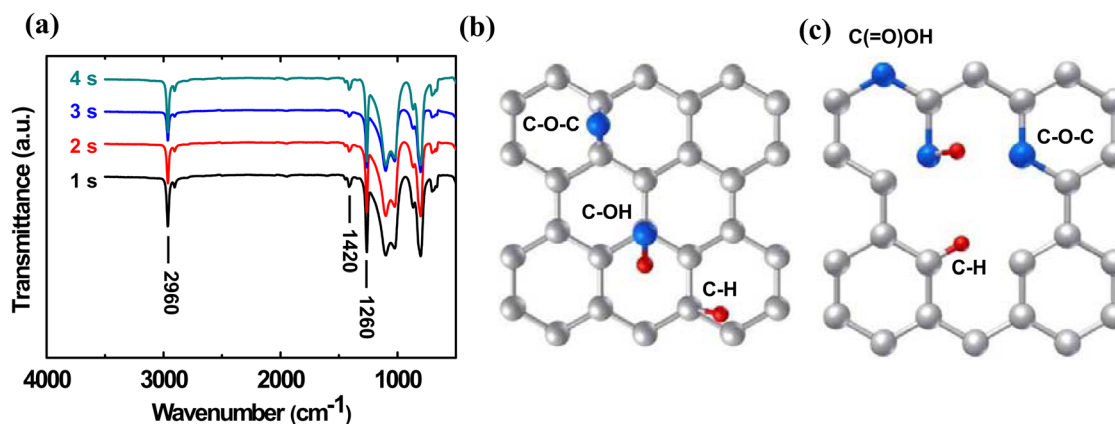


FIG. 3. (Color online) (a) FT-IR spectra of Ar plasma treated graphene taken from 3500 to 500 cm^{-1} . The characteristic vibrations that make graphene hydrophilic are the C-H stretching peak at 2960 cm^{-1} , the in-plane O-H bending peak at 1420 cm^{-1} , and the C-O-C anti-symmetric stretching peak at 1260 cm^{-1} . (b),(c) Schematic diagrams of the postulated atomic structure for graphene modified by Ar plasma treatment (large spheres: oxygen atoms; small spheres: hydrogen atoms). (b) C-O-C, C-OH, and C-H with sp^3 hybridization. (c) C([dbond]O)OH, C-O-C, and C-H with vacancies leading to dangling bonds.

Ar plasma. The changes in the Raman spectrum resulting from the Ar plasma treatment were similar to those induced by the O_2 plasma treatment, which shows that the transitions on the graphene surfaces caused by Ar and O_2 plasma can be explained by the same mechanisms.¹⁵ Figure 2(b) shows the Raman spectrum obtained from graphene protected by the patterned PR between the source and the drain. The results show that the protected graphene remains almost pristine despite the plasma treatment.

Figure 3(a) shows the FT-IR spectra of the graphene surfaces after the Ar plasma treatments. The new functional groups adsorbed on graphene could be identified. The characteristic vibrations are the C-H stretching peak at 2960 cm^{-1} , the in-plane O-H bending peak at 1420 cm^{-1} , and the C-O-C anti-symmetric stretching peak at 1260 cm^{-1} .¹⁶ These functional groups that are linked to carbon atoms in the ambient atmosphere can change the graphene surface from hydrophobic to hydrophilic because of the stronger interactions with water molecules (hydrogen bonding) than with carbon atoms (Van der Waals bonding).

Figures 3(b) and 3(c) show schematic diagrams of the postulated atomic structure of the graphene modified by Ar plasma. There are two points of analysis for the transition on graphene. (i) As shown in Fig. 3(b), sp^3 hybridized bonds of carbon atoms are formed with the breaking of π -bonds due to ion bombardment from the Ar plasma. This process should occur easily because the ion energy (the usual plasma potential energy is >10 eV) exceeds the π -bonding energy of carbon (2.7 eV).¹⁷ This agrees with the decrease in conductivity because the electrons are trapped by the formation of bonds with functional groups. (ii) As shown in Fig. 3(c), vacancies result in dangling bonds that are generated by the breaking of σ - (3.6 eV) (Ref. 17) and π -bonds. The sp^2 hybridization of graphene was transformed to sp^3 in the previous case, whereas the sp^2 hybridization was maintained because the original sites of carbon atoms were substituted by functional groups. Although the sp^2 lattice structure was maintained, the reason for the decrease in conductivity can be explained by interference from the breakage of planar sp^2 symmetry, which is induced by vacancies and dangling bonds.

Figure 4(a) shows the changes in the contact angle after the Ar plasma treatment (black squares). The non-plasma treated graphene shows hydrophobic properties at 83.2°. The graphene became more hydrophilic with increasing plasma treatment time. These transitions were attributed to new functional groups that adsorbed on the carbon atoms after the breaking of σ - and π -bonds, as mentioned previously. The graphene that was plasma-treated for 4 s was annealed at 200 °C for 10 h in an Ar atmosphere in order to ensure that the graphene would contain hydrogen, oxygen, and hydroxide. After annealing, the contact angle was restored to 78.5°, which is similar to the state of pristine graphene. The thermal energy can eliminate the functional groups and make graphene hydrophobic again. The yields of the intact electrodes were measured in order to confirm that functionalized graphene interacts more actively with metals, as shown in Fig. 4(a) (blue circles). In the case of non-plasma-treated graphene devices, only 4% of the electrodes maintained their original shapes; the others peeled off or were damaged [Fig. 4(b)]. In contrast, the plasma treatment improved the adhesion between graphene and electrodes, which increased the yield of the intact electrodes, even though no buffer layer had been used [Fig. 4(c)]. With increasing plasma treatment duration, more electrodes maintained their original shapes. No significant difference was observed over 2 to 4 s.

For device applications using graphene, the deposition of electrodes is a critical processing step, considering that the properties of graphene can be transformed (e.g., mobility, doping level) by the adsorption of metal atoms.^{18–20} For example, it is difficult to deposit electrodes with weaker interactions with graphene than Ti, such as Al, Au, Pd, etc., without a buffer layer. The binding energies of Pd with carbon, hydrogen, and oxygen are 1.7, 3.0, and 4.0 eV, respectively.^{21,22} FT-IR showed that functional groups were incorporated into graphene after the plasma treatment, which leads to a stronger interaction with the Pd electrodes because of the higher binding energies. This analysis is consistent with the experimental results and suggests that the deposition of electrodes is facilitated without buffer layers because the binding energies between most transition metals and H or O

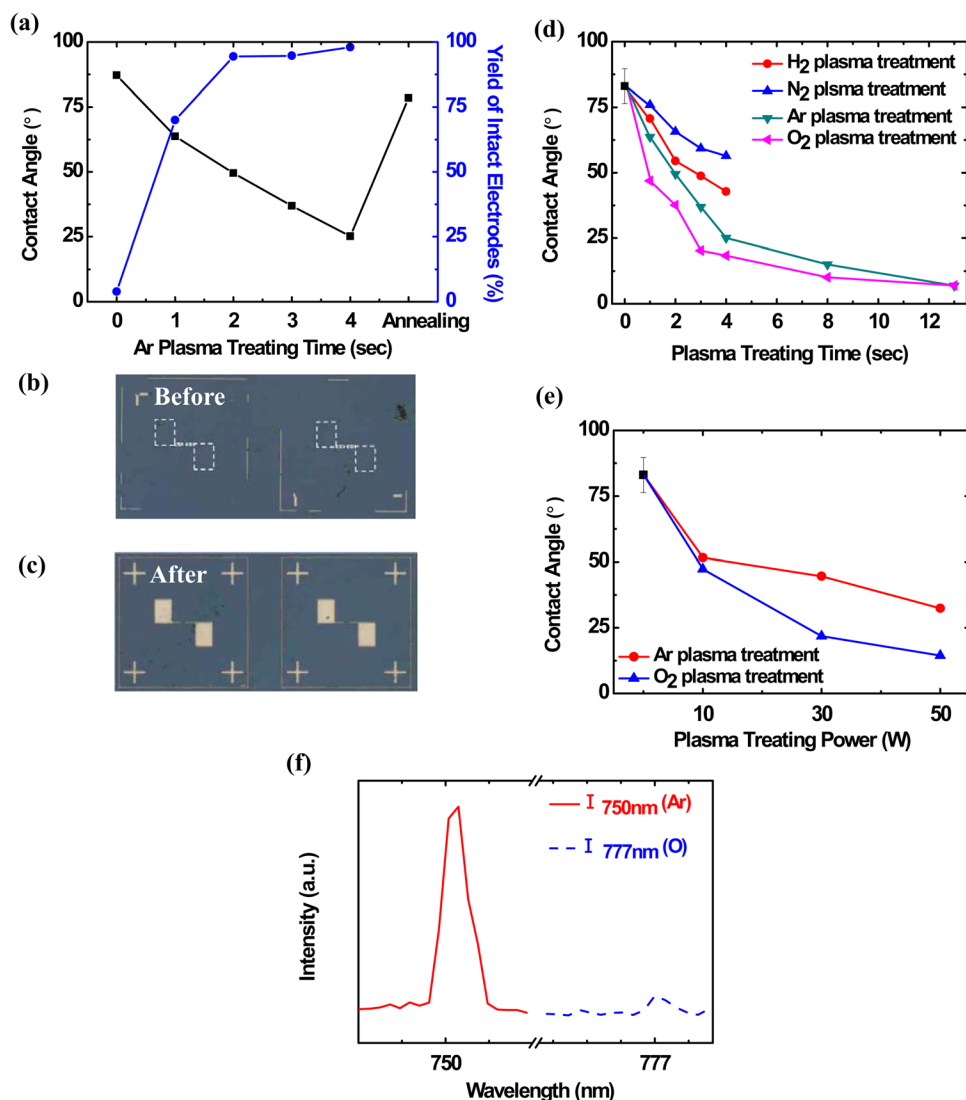


FIG. 4. (Color online) (a) Contact angles and yield of intact electrodes vs Ar plasma treatment time. (b),(c) Optical images before and after plasma treatment, respectively. (d) Contact angles vs plasma treatment time for various plasmas. (e) Contact angles vs plasma treatment power using Ar and O₂ gases. (f) Intensity of photons for Ar and O₂ plasmas under identical bias conditions.

are similar to that of Ti-C (2.9 eV).²² These observations and analyses suggest that the application of various metals in order to transform graphene properties is feasible. In addition, we can avoid the deposition of buffer layers (e.g., Ti, which can form titanium carbide) that leads to the formation of new layers at the graphene surface.²³

In order to verify the chemical and physical effects, plasma treatments were performed using a range of gases (Ar, O₂, N₂, and H₂) under identical bias conditions, as shown

in Fig. 4(d). The contact angles obtained from all plasma processes decreased with increasing processing time. H₂ plasma was the least effective in decreasing the contact angles of graphene surfaces, and O₂ was the most effective. Note that chemical reactions caused by radicals and physical bombardment by ions occur simultaneously during plasma processing. In the case of the H₂ and N₂ plasmas, the chemical reaction is not believed to have been very active. Physical ion bombardment from Ar plasma is more effective than that

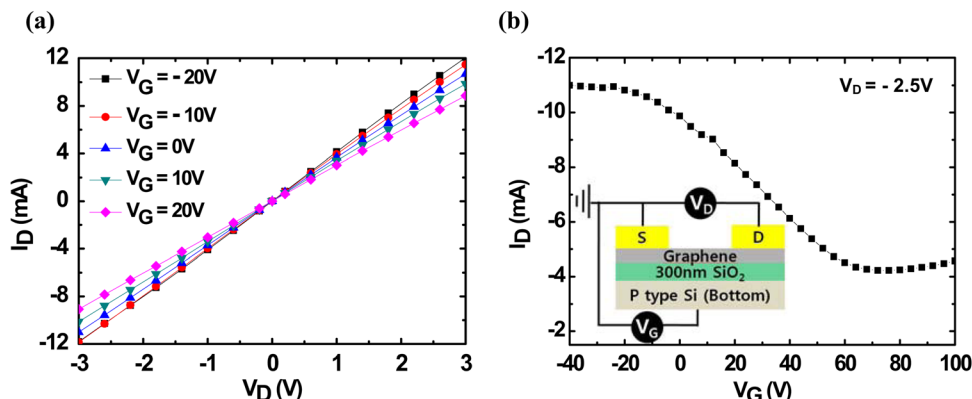


FIG. 5. (Color online) The electrical properties of a back-gating FET using pristine graphene. (a) I_D-V_D and (b) I_D-V_G indicate properties similar to those of pristine graphene reported earlier. P-type characteristics, which can be induced by defects or residues, were observed. The estimated hole and electron mobilities for V_D = -2.5 V were ~6500 and 1100 cm²/Vs, respectively.

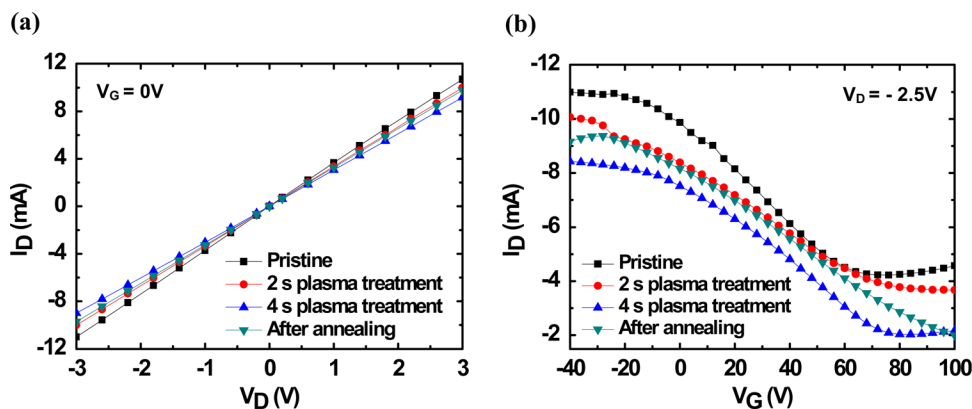


FIG. 6. (Color online) The electrical properties of pristine and plasma treated back-gating FETs for 2 and 4 s using graphene synthesized under the same conditions. (a) I_D - V_D for $V_G = 0$ V and (b) I_D - V_G for $V_D = -2.5$ V indicate that the plasma treatment has a weak influence on the electrical properties. The estimated hole mobilities for the pristine, 2 s, and 4 s plasma treated devices were 6500, 4500, and 5200 cm^2/Vs , respectively. After the 4 s plasma treated device was annealed at 200 $^\circ\text{C}$, the drain current level recovered slightly to that of the pristine sample.

with the other gases, as inert Ar has the largest ion mass and does not involve any chemical reactions. A comparison of Ar and O_2 plasmas revealed O_2 plasma to be more chemically reactive with graphene and able to lead to its effective removal. After 13 s of treatment, the graphene was etched away by both gases. In addition, Fig. 4(e) shows that the O_2 plasma is more effective than Ar with increasing plasma treating power. Figure 4(f) shows the relative photon intensities of the Ar and O_2 plasmas under identical bias conditions, which were measured using optical emission spectroscopy. Although the emission intensity of Ar is higher, the decrease in the contact angle is lower with the Ar plasma than with the O_2 plasma, which suggests that the chemical reaction is more effective in making graphene surfaces hydrophilic. According to these results, the extent of the transition of graphene surfaces can be controlled using a variety of gases, and the optimum conditions for enhancing the adhesion of graphene to metals and the transition of graphene properties can be determined.

Figure 5 shows the electrical properties of a back-gating FET using pristine graphene ($t_{\text{ox}} = 300$ nm, $L = 10$ μm , and $W = 5$ μm). The drain current (I_D) decreased with increasing gate voltage (V_G) when $V_G > 0$, as shown in Fig. 5(a). Figure 5(b) presents the transfer characteristics for $V_D = -2.5$ V and shows ambipolar and p-type characteristics, and the inset shows a cross section of the tested device. The p-type characteristics might be induced by hydrogenation and oxidation or by the reaction with residues during the device fabrication. The hole and electron mobilities were 6500 and 1100 cm^2/Vs , respectively, according to $\mu = (1/C_{\text{ox}})|d\sigma/dV_G|$ ($C_{\text{ox}} = 1.15 \times 10^{-8}$ F/ cm^2 for 300 nm SiO_2). The lower mobility for electrons than for holes might be due to electron scattering, which is affected by the high hole doping concentration, functional groups, and residues.^{24–26}

In order to confirm the effects of the plasma treatment on the source and drain, three different back-gating FETs were fabricated using the graphene under the same conditions. Figure 6 shows the electrical properties of pristine and 2 and 4 s plasma-treated graphene FETs. Figures 6(a) (I_D - V_D for $V_G = 0$ V) and 6(b) (I_D - V_G for $V_D = -2.5$ V) indicate that the plasma treatment has a minor influence on the electrical properties, as the active channel region is protected by PR. The estimated hole mobility for the pristine and the 2 and 4 s plasma treated devices was 6500, 4500, and 5200 cm^2/Vs ,

respectively. Compared to the results reported by Liang *et al.* (hole mobility of 3735 cm^2/Vs), the hole mobility was higher despite the plasma treatment. After the 4 s plasma treated device was annealed at 200 $^\circ\text{C}$, the drain current level recovered slightly to that of the pristine sample. The defects were removed by the thermal energy, which can lead to a decrease in the number of dangling bonds that capture or scatter the electrons. High performance graphene devices can be fabricated with better adhesion between graphene and the electrodes by applying this plasma treatment technique.

IV. CONCLUSION

This study examined the effects of various plasma treatments on the adhesion between graphene and electrodes. After the plasma treatment, functional groups, such as hydrogen, oxygen, and hydroxide, which make the graphene surface hydrophilic, were formed. The contact angle showed a hydrophobic to hydrophilic transition of graphene with increasing plasma treating time. The estimated hole mobility for the 4 s plasma treated devices was 5200 cm^2/Vs . This indicates that the plasma treatment on graphene is quite effective for fabricating graphene FETs without the need for buffer layers.

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