Edge contacts of graphene formed by using a controlled plasma treatment†

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Despite the fact that the outstanding properties of graphene are well known, the electrical performance of the material is limited by the contact resistance at the metal–graphene interface. In this study, we demonstrate the formation of ‘edge-contacted’ graphene through the use of a controlled plasma processing technique that generates a bond between the graphene edge and the contact metal. This technique controls the edge structure of the bond and significantly reduces the contact resistance. This simple approach requires no additional post-processing and has been proven to be very effective. In addition, controlled pre-plasma processing was applied in order to produce CVD-graphene field effect transistors with an enhanced adhesion and improved carrier mobility. The contact resistance attained by using pre-plasma processing was 270 Ω μm, which is a decrease of 77%.

Introduction

Graphene is a two-dimensional (2D) material that exhibits unique properties,1,2 such as a very high intrinsic mobility,3,4 and it has drawn attention as a potential material for use in next-generation semiconductor devices. The applicability of graphene has been demonstrated in radio frequency (RF) devices,5,6 field effect transistors (FET),7 ultrafast photo-detectors,8 and flexible, transparent electronics.9,10 Recently, large-scale synthesis of graphene was successfully achieved via chemical vapor deposition (CVD) with metal catalysts,11,12 and this will potentially allow for the industrialization of graphene.

Nevertheless, the metal–graphene (M–G) interfaces have an inherent problem in that carrier transport is generally obstructed,13–17 impeding further improvements in the performance of graphene devices.18–21 In ordinary surface contacts at the M–G interface, carrier injection takes place from the metal into the underlying graphene and is followed by carrier transport into the channel region.19 However, the contact resistance (Rc) is understood to be mainly determined by the chemical bonds, the electronic structures at the M–G interface, and the geometric structure of the interface, including both the surface and edges of the graphene. Therefore, the differences in the surface and edge contacts at the M–G interface should be considered to develop an efficient and reliable process that can minimize Rc and enable efficient charge transport at the M–G interface.

In general, Rc can decrease by either modifying the fabrication process or by performing pre- and post-treatment of graphene.

In the first approach, the fabrication process is modified in order to efficiently improve the adhesion of the M–G contact. Franklin et al. studied graphene fabrication with a double contact geometry that consists of metal layers below and above the graphene layer, and they experimentally demonstrated a decrease in Rc of at least 40%.22 Smith et al. cut graphene in order to pattern the contact area, facilitating adhesion by forming partial edge contacts in the contact regions, and this method resulted in 32% reduction of Rc.23 Palacios et al. used a sacrificial layer made of Al to improve the surface roughness of graphene, and they obtained an Rc of 0.2–0.5 kΩ μm.24 Wang et al. used hexagonal boron nitride (hBN) to encapsulate graphene, forming a sandwiched structure with a total edge contact that showed an Rc of 0.1 kΩ μm.25 Researchers have also applied various forms of pre-treatments and post-treatments on graphene, which is the second approach. For example, ultraviolet (UV)25 sensitive polymers can contaminate the graphene surface during fabrication, adversely affecting the M–G contacts. Therefore, post-treatments can be essential in reducing polymeric residues that can deteriorate contact properties. Thermal annealing and plasma treatments have been confirmed to be effective to these ends,26,27 and post-annealing treatments have also been reported to form edge-contacted graphene.28 Furthermore, our previous study demonstrated that post-plasma treatment at a lower power (Ar, O2, N2 and H2)21 is effective in reducing Rc, with the additional advantage of operating at a low tempera-
ture with a large scale plasma system, which makes the process compatible with current semiconductor device processing. We transformed the graphene surface from hydrophobic to hydrophilic, and we also generated defects that improved the adhesion between the M–G interface and decreased $R_c$. However, post-treatments generate defects and induce a significant loss of graphene, giving rise to a reduction of the current for G-FETs. Furthermore, these additional processes increase the cost of graphene production. Recently, $R_c$ has been improved by theoretically simulating edge-contacted graphene,29–32 and further contributions based on these simulations have improved the formation of edge contacts.20,24,33

In this study, we explored the use of a pre-plasma process in order to enhance bonding and coupling at the M–G interface with an edge-contact configuration. Hundreds of CVD-graphene back-gated FETs were fabricated, and electrical measurements were performed in order to confirm the validity of the proposed process. The lowest value measured for $R_c$ in the devices was found to be 270 Ω μm, when they were measured by using the transfer length method (TLM). The results of the experiments indicate that the proposed pre-plasma treatment can provide a new edge-contact method that can significantly improve the performance of graphene devices.

Pre-plasma processing for “edge-contacted” graphene

Large-scale device processing was achieved by synthesizing graphene via CVD on thin copper foils loaded in a vacuum furnace at a temperature of 1000 °C. After spin coating a PMMA solution onto the graphene, the foils were post-baked at 120 °C for 5 min in order to improve the adhesion of the polymer and to remove the remaining solvent in the copolymer. The other side was etched using inductively coupled O₂ plasma (gas flow, 30 SCCM; power, 20 W; time, 10 s). The PMMA/graphene was removed from the top of the copper films by dipping them into an ammonium persulfate solution (0.05 g ml⁻¹) for 8 h. The PMMA/graphene films were cleaned with DI water before transferring the graphene onto polished Si wafers by using a 300 nm-thick thermally grown SiO₂ layer. The PMMA/graphene/SiO₂(300 nm)/P–Si wafers were dried for 2 h in an air hood and were annealed at 110 °C for 5 min to remove the remaining water molecules. The PMMA was then removed with the use of acetone steam at 130 °C. Fig. 1(A) shows the TLM patterns that were formed after photolithography with a positive photoresist, and an image obtained with an optical microscope (OM) is shown in Fig. S1(A).†

Pre-plasma processing is different from conventional processes in that an edge contact is generated, which is the key result of this study. In our previous study, low power plasma was used to clean a few-layered graphene (FLG) surface, and no defects were generated in the FLG graphene.34 In this study, high ion-energy plasma was used to etch graphene. An optimized pre-plasma processing condition was obtained after various trials with different gas conditions (H₂, Ar, N₂, etc.) and different power levels. Fig. 1(B) shows the schematics of the plasma processing apparatus that was used to generate capacitively coupled plasma (CCP) at a low power of 25 W with an O₂ flow rate of 30 sccm. The actual working pressure of the chamber was set to 30 mTorr, and the graphene was subsequently exposed to plasma for durations of 5, 15, 25, 35, 45, 55, and 65 s. Fig. 1(C) and S1(B)† show the sample after exposure, and when compared to Fig. S1(A),† the graphene can be observed to have been cleanly etched and to have formed a complete edge contact.

After plasma processing, Cr–Pd–Au (1 nm/15 nm/50 nm) was deposited via electron beam evaporation. The metal/PR layers were removed with hot acetone at 50 °C, and photolithography was used again to provide channel definition. Fig. 1(D)
and S1(D)† show the final structure of the device with the patterned graphene that was used for the electrical test. We measured the electrical properties of the devices at room temperature by using a semiconductor analyzer (Agilent 4155 C).

**Measurements of \( R_c \) from graphene with a controlled edge**

The measurements were performed for two sets of five transistors. The designed TLM structures that were fabricated on one sample are shown in the insert of Fig. 2(A). The OM image also proves that the device structure was patterned with a graphene channel width (\( W \)) of 30 μm and a channel length (\( L \)) that varies from 10 to 50 μm, in increments of 10 μm. In addition, other patterns with \( L = 5, 10, 15, 20 \) and \( 25 \) μm were also used in this study. We first performed two-terminal electrical measurements without applying a back gate voltage. The source–drain current for all the five graphene devices is plotted as a function of the source–drain voltage in Fig. S2(A), and S2(A) and (B)† indicate that the resistance consistently increases as \( L \) increases.

![Graph showing measurements of \( R_c \) from graphene with a controlled edge](image)

The TLM method was used to extract \( R_c \), under the assumption that in a diffusive regime, \( L \) is much larger than the carrier mean free path. Therefore, the total resistance \( R_{\text{total}} \) can be written as

\[
R_{\text{total}} = \frac{2R_c}{W} + \rho L \ [\Omega]
\]

where \( R_c \) is the contact resistance, \( W \) is the channel width, \( L \) is the channel length, and \( \rho \) is the 2D channel resistivity. \( R_{\text{total}} \) versus \( L \) are plotted with linear fits in Fig. S3,† along with the associated equations for the exposure to oxygen plasma with durations of 5 (Fig. S13†), 15, 25, 35, 45, 55, and 65 s. We extracted \( R_c \) directly from the \( y \)-intercept of the \( R_{\text{total}} \) vs. \( L \) curve by using the confidence fit equation and multiplying the \( y \)-intercept to \( W = 30 \) μm.

20 devices were fabricated in order to obtain the results seen for the six figures shown for each condition in Fig. S3.† The duration of the exposure to O₂ plasma increased from 15 to 45 s and resulted in a ~77% decrease in \( R_c \). A 90% fitting confidence shows that the average decreased by 71% with the lowest \( R_c \) of 270 Ω μm, which is close to the lowest \( R_c \) reported for CVD-graphene at room temperature. Note that most of the \( R_c \) results that were presented in the previous reports fall in

![Fig. 2: Diagram showing changes in \( R_c \) for plasma treatment for 15 and 45 s and different gate modulation. Inset: optical image of the designed TLM structure with five transistors. (B) Contact resistance versus processing time, showing a large reduction in \( R_c \) at 35 to 45 s. (C) The structure after 5–10 s, during which graphene cannot be etched. The purple and red structures indicate graphene with a photoresist and graphene undergone plasma treatment, respectively. (D) The edge of graphene varies with the plasma treatment time. The exposed graphene contact length (\( L_{\text{exposed}} \)) changed from longer to shorter. (E) The geometry of the “edge-contact” formed via a pre-plasma process. (F) A structure with over-etching, in which the contact between the metal electrode and graphene is reduced.](image)
the range between 300 and 1000 Ω μm. Since this value was obtained for two-terminal devices, it includes an intrinsic limit imposed by the quantum resistance of the channel. Despite this limitation, the proposed pre-plasma processing with an edge-contact structure gives rise to a larger improvement in $R_c$ for the CVD-graphene device. Fig. S4† summarizes some of the figures of merit in order to compare the performance that was obtained from devices fabricated with plasma exposure times of 5, 15, 25, 35, 45, 55, and 65 s. We obtained a reduction for $R_c$ of 77% as a maximum from devices exposed to oxygen plasma for 45 s. Meanwhile, the results obtained for the 5 s O₂ plasma condition were not considered because the graphene surface cannot be completely etched within the plasma induction time, leading to a high $R_c$ (Fig. S12–13†). Fig. 2(A) and 2(B) show the gate dependence of $R_c$ for the CVD-graphene device. Fig. 2(A) shows the gate dependence of $R_c$, and a relatively low $R_c$ was attained for devices treated with plasma for 45 s.

Fig. 2(B) shows significant reductions in $R_c$ when pre-plasma processing is used for various durations. An improvement in $R_c$ can be clearly seen, and the improvement is more pronounced at exposures for 35 and 45 s, which as a result are found to be the most suitable O₂ plasma etching times for the graphene edge-contact shown in Fig. 2(C)–(F). Consequently, the controlled plasma process is related to the surface contact resistance ($R_c$), and a structural variation is shown according to the plasma exposure time, which involves etching of graphene induced at the G–M interface. The ideal contact structure was observed from a condition between 35 and 45 s of exposure to O₂ plasma, where a minimal $I_{exposed}$ was obtained.

We used SEM to investigate the changes on the edge of the graphene by analyzing the graphene patterns that resulted from the increase in the plasma treatment time. Fig. S8† shows a line of best fit for $L$ with respect to the measurements of the development in the edge of the samples treated with plasma for 15 to 45 s. Fig. S7(E)† shows SEM images of graphene films treated with controlled plasma for 15, 45, and 100 s, showing an obvious variation in $L$. When the linear fit for $R_c$ and the channel length are compared, as shown in Fig. S5 and S8† they match each other. We also performed SEM measurements to measure the variation of PR in vertical and lateral directions. Fig. S15† shows the variation of the polymer (PR). According to the results, during the oxygen plasma etching process, graphene is more easily etched than the polymer (PR) in both vertical and lateral directions. Therefore the structural variation shown in Fig. 2(C)–(F) is supported, and this verifies our assumption that the controlled plasma treatment can improve the edge structure by facilitating the edge contact. We showed the partial over-etching areas along the edge in Fig. 2(F). Consequently, the controlled plasma process is different from conventional processing in that the edge contact can be maximized with precision and simplicity, minimizing the surface contact and requiring no additional post-processing to generate defects.

We performed further tests to elucidate the mechanism through which the proposed treatment leads to a lower $R_c$. Raman analyses were used to examine the effects of the plasma treatment on the edge of the patterned graphene covered with a PR pattern followed by removal with acetone. Fig. S7(C)† shows the pattern produced by the sample used in the Raman analysis. Here, the Raman analysis of samples treated with plasma for 15, 35, and 65 s shows that those times show sufficient variations in the defects of the graphene edge. The Raman spectra in Fig. 3(A) were obtained at the edge of the graphene after plasma treatment for 15, 35, and 65 s. Three clear D-band signals were observed at the graphene

Mechanisms of the pre-plasma process leading to low $R_c$

There are several reasons for which the proposed plasma pre-process can produce a low $R_c$. First, the Cr adhesion layer for the asymmetrical metallization structure is crucial because the work function of Cr is 0.16 eV lower than that of graphene. More importantly, the proposed controlled plasma treatment generates some additional interfacial species, and also increases the chemical binding energy and the charge transmission. The covalent/ionic bonds that are formed between the metal and carbon atoms, which are stronger relative to the weak van der Waals bonds generated under a conventional top contact, give rise to a lower $R_c$. Furthermore, we find that the edge structure is greatly improved when using our controlled plasma process. The graphene can be etched to expose the edges, forming contacts with a smaller distance between the graphene edge and the metal contact edge ($I_{exposed}$). The metal contact edge shown in Fig. 2(C)–(F) is related to the surface contact resistance ($R_c$), and a structural variation is shown according to the plasma exposure time, which involves etching of graphene induced at the G–M interface. The ideal contact structure was observed from a condition between 35 and 45 s of exposure to O₂ plasma, where a minimal $I_{exposed}$ was obtained.
edge, and a disorder-induced Raman signature (D-band signal) that emerged at the three kinds of the graphene edges suggests that our controlled plasma treatment generates defects.

It is reported that the edge contacts lead to a shorter bonding distance that can contribute to larger orbital overlap compared to surface contacts, due to different natures of the bond mechanism. The C–C bonding in graphene is expected to be replaced in part with C–O bonds, and the number of C–O bonds increases as the oxygen plasma treatment time increases. Incorporation of interfacial species such as O, which passivates the graphene edge before formation of metal contacts, is known to enhance the transmission. We think that the edge contact with an O termination is responsible for the that is smaller than that with a C termination. Moreover, the D-band in Fig. 3(A) reveals that the modification induced by the oxygen plasma treatment begins at ~15 s and is most effective at ~35 s.

The changes in the edge gradually disappear when the time is > ~65 s, and the temporal changes that occur at the edge can be described in the following steps. First, plasma treatment for a short time results in initial damage and in etching of the graphene. Then, more broken sp2-hybridized C–C bonds are generated. Finally, the edges are cleaned and etched again. Therefore, when graphene is patterned with ~35 s of oxygen plasma treatment, the edges become more reactive and more susceptible to bonding with other materials.

Fig. 3(B), (C), and (D) present the spatial Raman intensity maps of the D-, G- and 2D-bands of the graphene flakes after plasma treatment for 15, 35, and 65 s. In terms of the three pictures of the D-band, the edge-defects are more clearly seen in Fig. 3(C) of the patterned graphene treated with plasma for 35 s. The defects, or the dangling bonds in the CVD-graphene edge, are easier to generate because they have an imperfect lattice and grain boundaries. With respect to our plasma treatment mechanism, the C–C bonds that break on the edge result in dangling carbon bonds that react directly with the metal atoms in the end-contact geometry. After metal deposition on CVD-graphene, the metal–graphene contact improves due to the presence of the defects and the dangling carbon bonds. These results corroborate that the controlled plasma treatment can generate defects and dangling bonds, and the treatment dramatically improves the metal–graphene chemical reaction in the end-contact geometry, and this explains why decreases in graphene devices after the controlled plasma treatment.

Carrier transport at surface and edge contacts

We then compared the carrier transport process between the surface-contact and the edge-contact. We selected Cr as the wetting electrodes since these can form strong interfacial coupling bonds and assist with defects produced through the proposed controlled plasma treatment. The proposed treatment plays a vital role in forming covalent bonds between the metal and the graphene edge. Meanwhile, the end-contact structures with reactive graphene edges, as well as with structural disorders and amorphized edges, were formed through the controlled plasma treatment. This facilitates for the carbon sp3 orbital for σ bonding and the metal d orbital to couple cohesively. That is, the end-contact electrodes lead to a greatly increased interaction energy compared to that of side contact electrodes. The graphene edge contacts can achieve a very low , due to the short binding distances (coupling length) and strong overlap in the electron orbitals, and are superior to side contacts. The union of the wetting metal (Cr), the improved end-contact structure, and the reactive, disordered graphene edges enhance carrier transmission between the metal and graphene through a strong hybridization and a reduced coupling length.

Fig. 4(A) and (B) show the energy band structure at the surface-contact and at the end-contact junction, respectively.
We expect a larger coupling length between the metal and the graphene for the surface-contact to graphene because of the presence of stable π-bonds without any dangling bonds. However, for the end-contact junction, the covalent/ionic bonds that are formed between the metal and the carbon atoms enable a lower $R_c$, as compared to the weak van der Waals bonds formed in a conventional top contact. Furthermore, the Cr-graphene edge contact has been found to have a shorter binding distance ($0.64-1.44$ Å) and larger binding energies (3.4–6.8 eV per carbon) relative to Cr-graphene side contacts, for which the binding distance is $\sim 1.83-2.02$ Å and the binding energies are $\sim 0.32-0.75$ eV per carbon. Therefore, the proposed controlled plasma treatment gives us a way of breaking the stable π-bonds, while the dangling σ-bonds are formed. That is, the wetting metal and the improved end-contact structure increase the binding strength and reduce the coupling length, which is in agreement with the quantum mechanical interpretation of end-contacts and surface-contacts presented by Matsuda et al. A summary of some of the key metrics that compare the surface contacts and the edge contact junctions is given in Fig. 4, Table (C).

![Diagram](A) Energy band and electronic structures for surface contact. (B) Energy band and electronic structures for end contact. $\Phi_M$ for Cr is $\sim 4.6$ eV. (C) Metrics comparing the end contact and surface contact junctions.

We explored the properties of metal–graphene contacts in simulation that takes into account the mechanisms and comparison of carrier transport on the surface and edge contact junction, for $R_c$ at $T = 300$ K. The lowest $R_c$ of 270 $\Omega$ $\mu$m was demonstrated with the use of Cr metal at the end of the contact structure, enhancing the carrier transport of CVD-grown graphene for use in electronic devices. This controlled pre-plasma treatment is compatible with the current large-scale electronic device processes, and it is therefore expected to be a baseline process for fabrication of high-performance CVD graphene and 2D devices.

### Conclusion

A process that uses oxygen pre-plasma during graphene device fabrication produced a controlled edge-contact structure that reduced $R_c$ by as much as 77%. The lowest $R_c$ of 270 $\Omega$ $\mu$m was demonstrated with the use of Cr metal at the end of the contact structure, enhancing the carrier transport of CVD-grown graphene for use in electronic devices. This controlled pre-plasma treatment is compatible with the current large-scale electronic device processes, and it is therefore expected to be a baseline process for fabrication of high-performance CVD graphene and 2D devices.
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References