Large-Scale Graphene Oxide Sheets by Low Damage Plasma Treatment

Hsiang-En Cheng¹, Ching-Yuan Su² and Chi-Hsien Huang¹

¹Department of Materials Engineering, Ming Chin University of Technology, New Taipei City, Taiwan
²Graduate Institute of Energy Engineering, National Central University, Taoyuan, Taiwan

chhuang@mail.mcut.edu.tw

Abstract

Although graphene is a promising material for a variety of applications, the development of graphene-based devices will require higher control over its surface functionalization. Plasma treatment is a major tool in VLSI processes that can react chemically with various materials. A number of groups have used plasma treatment to functionalize graphene surfaces. However, even multilayer graphene can be etched away within a few seconds in a conventional plasma environment due to the presence of energetic ions and vacuum ultraviolet (VUV) irradiation [1,2]. Both species in plasma have energy higher than that of the C–C bonds of sp²-hybridized C atoms in graphene, thereby easily breaking the lattice of graphene and destroying the honeycomb-like C nanostructure. As a result, the etching rate is generally too fast to allow precise control of functionalization. To overcome this issue, we developed a method—low-damage oxygen plasma treatment (O–LDPT) to functionalize CVD-grown graphene sheet. As shown schematically in Fig. 1, by inserting a complementary filter into a parallel plate plasma system, the ions and VUV can be efficiently shielded by the filter, allowing only radicals, which have the highest reactivity among plasma-generated species, to diffuse through the filter with extremely low kinetic energy and reach the nanomaterials to gently functionalize them [3]. Raman and XPS measurements revealed that oxidative functionalities were formed on the graphene surfaces in a highly controllable manner, as shown in Fig. 2 and 3, respectively, through variation of the treatment time ranging from 0 to 7 min. Contact angle (CA) measurements exhibited the high hydrophilicity (CA ~23°) of the large-scale graphene after O–LDPT while maintaining the featured bands of graphene in the Raman spectra.

We confirmed that low damage occurred during this process by exposing double-layer graphene (DLG) samples to O-LDPT and then measuring their current-voltage (I–V) characteristics. We fabricated two-terminal devices with oxidized DLGs as the channel, as presented schematically in the inset of Figure 5. For comparison, the devices with DLGs O₂-plasma were also prepared. The representative I–V curves of devices with various conditions as displayed in Figure 5. The I–V curve of the DLG that had not been subjected to treatment was linear, indicating conductive characteristics. The current level of the untreated SLG was almost identical to that of the DLG (not shown here). First, we examined the degree of oxidation after conventional plasma treatment using the same processing conditions for 1 min. The current level decreased dramatically. On the contrary, after exposing the DLG samples to O-LDPT for up to 5 min, the I–V curves remained linear. These curves for the devices incorporating the oxidized DLGs all featured almost the same current level; in addition, these values were only slightly lower than that of the DLG that had not been subjected to oxidation. These results suggest that only the top graphene layer of the DLG was oxidized during O-LDPT, implying an ultra-low-damage plasma process even when the exposure time was as high as 5 min, thereby allowing the bottom graphene layer of the DLG to remain conductive. The result indicates that the bottom layer of the graphene sheet was almost unaffected, even when a massive number of oxidative functionalities had been introduced onto the top layer of the graphene sheet. When the treatment time reached 7 min, the current level decreased significantly, leading to higher electrical resistance. We believe that this relatively long treatment time resulted in more defects near the grain boundaries, where oxygen radicals preferentially attack boundary edges. It leads to diffusion of oxygen radicals through top graphene and reach the bottom graphene layer for partial oxidation.

Accordingly, our developed LDPT process is a promising technique for the surface modification of graphene, potentially enhancing its interfacial compatibility with the versatile dielectric materials employed nowadays in IC processes.

References

Fig. 1. (a) Schematic representation of the LDPT system. (b) Enlarged view of the dashed red rectangle in (a).

Figure 2: Representative Raman spectra as a function of treatment time.

Figure 3 (a) XPS spectra of SLG samples oxidized through O-LDPT for various treatment times.

Figure 4: Contact angles of oxidized SLG samples exposed to O-LDPT for various treatment times.

Figure 5: I-V curves of devices (inset) incorporating DLGs oxidized by O-LDPT for various treatment times.