Solid-phase and gas-phase oxidation of graphitic carbon thin films

Carbon has various allotropes including diamond and graphite, which exhibit quite different physical properties and chemical reactivity. For instance, graphite shows 10^{15} times larger electrical conductivity than diamond due to the existence of delocalized π electrons. Thus, it is expected that the electronic properties of carbon materials can be modified by controlling the ratio of sp^2/sp^3, and doping of atoms with different electronegativity into carbon is one route to realize sp^2/sp^3 control. Introduction of oxygen into graphitic carbon, consisting of highly and/or purely sp^2 hybridized bonds is a promising pathway, because oxygen can react with carbon to form stable carbon-oxygen bonds even in the ambient atmosphere.

So far, oxidized graphene has been synthesized mainly by a wet process developed by Hummers and Offeman (the so called as Hummers method). However, the Hummers method has been done under strong oxidation conditions, so that various functional groups such as epoxy, carboxyl, hydroxyl and carboxyl groups are introduced in a non-uniform manner.

In this study, formation of a carbon-oxygen bond and/or oxygen-containing groups has been examined using two different oxidation methods. One is solid-phase oxidation on oxide substrates, in which oxygen ions supplied from substrate react with carbon. The other is a novel oxidizing technique based on a solid-gas reaction using a reactive oxygen gas species. For the latter process, two atomic oxygen sources were utilized and one of them yields mildly oxidized graphene, which has a smaller variety of oxygen-containing groups and less disordering of carbon atoms in the graphene hexagonal lattice.
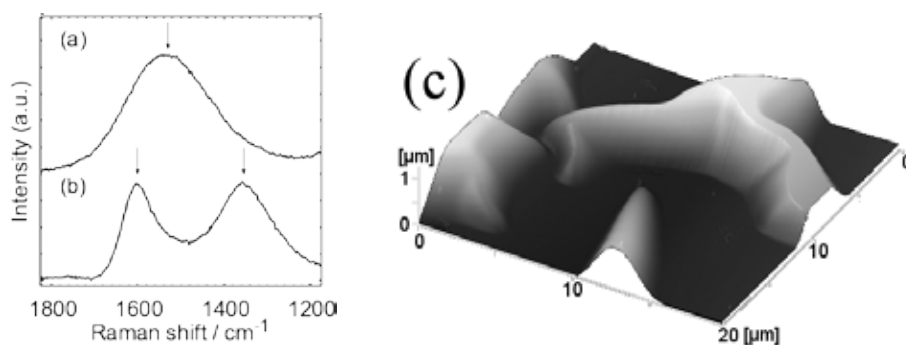
Fig. 1 Raman spectra from the sample (a) before and (b) after post-annealing (λ_{exc} = 532 nm). (c) A topographic image of the carbon film after post-annealing taken with AFM (20×20×1 μm).

Solid-phase oxidation of carbon thin films on oxide substrates by annealing at higher temperatures

Solid-phase oxidation of graphitic carbon thin films on oxide substrates at higher temperatures was investigated in order to dope oxygen atoms from the substrate to the film. 10 nm-thick carbon films were deposited on refractory oxide substrates such as yttria stabilized zirconia (YSZ), magnesium oxide and sapphire using the pulsed laser deposition technique (λ = 266 nm) in a vacuum chamber, which was followed by *ex-situ* annealing at higher temperatures, ranging from 1500 to 2700 °C under high vacuum and argon atmosphere conditions, respectively.

As-deposited carbon films showed a significant contribution from sp^3 according to the Raman spectrum (Fig. 1a). Successive post-annealing at lower temperatures below 1500 °C caused graphitization (conversion from sp^3 to sp^2), and nano-graphitic carbon films were formed (Fig. 1b). At higher annealing temperatures, a reaction occurs at the interface between the carbon film and oxide substrate, resulting in the exfoliation of the film from the substrate. This indicates that ionic oxygen continuously supplied from the substrate during the annealing is highly reactive and removes carbon atoms at the interface as gaseous CO/CO_2.

Graphene grown on metal surface by chemical vapor deposition

High quality graphene films with well-regulated numbers of layers were fabricated using the chemical vapor deposition (CVD) technique. As is well known, thin graphene layers are grown by decomposition of hydrocarbon gas and/or segregation of carbon at the surfaces of transition metals. In this study, copper was chosen as a substrate to obtain mono-/bi-layer graphene at the surface. Hydrogen and methane gases were introduced to a quartz tube as cleaning and source gasses, respectively. The process temperature, pressure and time were typically 1000 °C, 20 Pa, and 1–10 min, respectively. Characterization of graphene was carried out with Raman spectroscopy, scanning electron microscopy (SEM) and scanning tunneling microscopy (STM).

A Raman spectrum (excitation wavelength λ = 514, 532 and 633 nm) (Fig. 2) of the obtained film showed a sharp G peak at 1587 cm^{-1} and 2D peak at 2681 cm^{-1}. The full width at half maximum (FWHM) of the 2D peak is 48 cm^{-1}, indicating that mono- and/or bilayer graphene was obtained. The value of the 2D peak is fairly wider than those previously reported, 30 cm^{-1}. This broadening may be
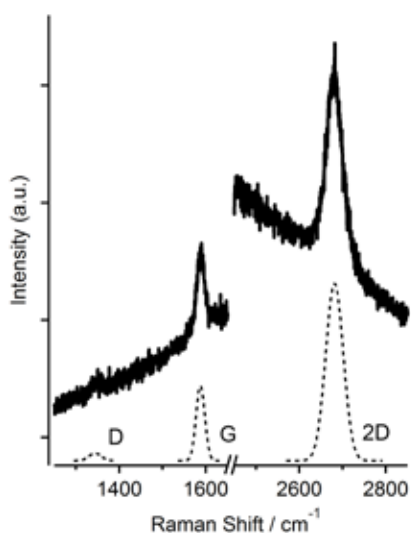
Fig. 2 A Raman spectrum of as-grown pristine CVD-grown graphene ($\lambda = 514$ nm). FWHM(2D) = 48 cm^{-1}. The dotted curves at bottom are curve-fitted peaks of D, G and 2D peaks. The intensity (area) ratio I(G)/I(D) is 13.4.
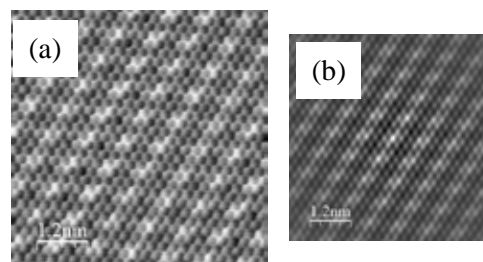

Fig. 3 Images of monolayer graphene grown on copper substrate taken by UHV-STM at 4.7 K: (a) topographic image and (b) auto-correlated image of (a). (V_{bias} = - 0.2 V, $I_{tunneling}$ = 2 nA.)
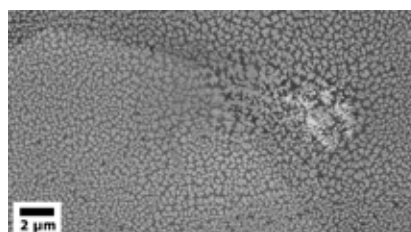

Fig. 4 An SEM image of as-grown graphene. Sub-micrometer bright regions correspond to sub-monolayer graphene islands.

due to orbital hybridization between graphene and the underlying copper or surface plasmon resonance of copper, which would modify the band structure of the graphene film. Even in the film deposited for the longer time of 30 min, the Raman spectrum did not essentially change, implying that the number of layers is limited to two irrespective of the deposition time.

Fig. 3(a) is an STM image taken on the graphene film, clearly resolving both an atomic honeycomb lattice and Moiré patterns with lateral size over 20 nm. From the observation of Moiré patterns, it can be concluded that monolayer graphene was grown in this region. Such the hexagonal lattice and Moiré patterns were reproducibly observed, indicating that monolayer graphene covers most of the films obtained here. SEM observations revealed that the graphene film is of polycrystalline form with grain sizes of sub-microns (Fig. 4). Thus, the density of grains can be estimated to be several per micrometer square. As a consequence, there are many grain boundaries, at which defects or edges, such as 5-/7-membered aromatic rings missing carbon atoms in the honeycomb lattice, might exist.

Atomic oxygen exposure to graphene for gas-phase oxidation

Gas-phase oxidation of graphene has been investigated in an ultra-high vacuum (UHV) chamber by irradiation of atomic oxygen to graphene grown on a copper surface. Two atomic oxygen sources were tried in an effort to confirm correlation in the dissociation ratio of oxygen species. The irradiation time was typically 5–15 min. During the irradiation of oxygen species, the graphene sample was not heated, in order to prevent from carbon etching. The Raman spectra of the oxidized graphene exhibited a sharp D peak centered at around 1350 cm^{-1} (Fig. 5). This D peak in the spectra was relatively narrower than that of unreduced graphene oxide prepared using the Hummers method
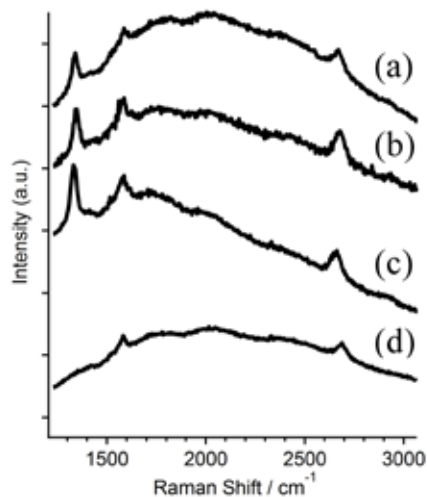
Fig. 5 Raman spectra of graphene after atomic oxygen exposed ((a, b, c) three spectra from three different points within the same sample) and (d) before exposed. (λ_{exc} = 532 nm, laser spot size: 1 μm) (FWHM(2D) = 37 cm^{-1})
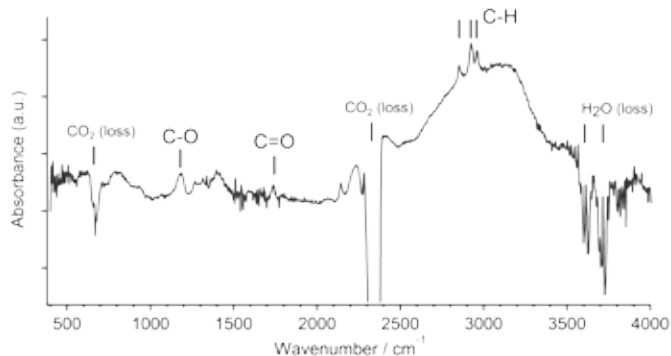

Fig. 6 Reflection infrared Fourier-transform spectrum of graphene oxidized by microwave-assisted atomic oxygen.
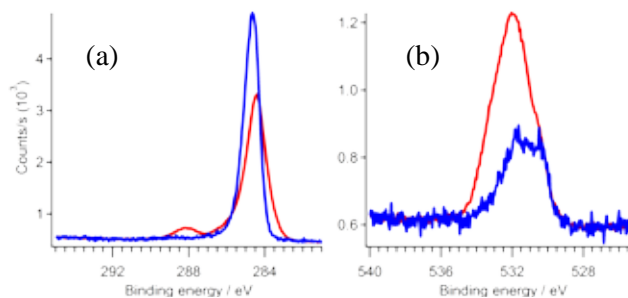

Fig. 7 Core-level X-ray photoelectron spectra of (a) C 1s and (b) O 1s. Blue and red curves correspond to those for graphene before and after oxidation. All spectra were collected at the same photon flux.

(FWHM: typically around 100 cm^{-1}) although there was little change in the G and 2D peaks.

Infrared spectroscopic and X-ray photoelectron spectroscopic studies revealed that this oxidation method allowed us to introduce oxygen atoms including both ether and carbonyl groups onto graphene. Notably, STM images of the presently prepared oxidized graphene showed a clear sp^2-based honeycomb lattice similar to those of pristine graphene before oxidization. Even after repeating the irradiation process, there was no significant difference in nanoscale topographic images. By combining all the results discussed above, it is likely that the oxidation occurs mainly at the grain boundary regions, because carbon atoms near edges or defects at the boundaries seem to be more reactive than those in the honeycomb lattice.

Summary

In this work, solid-phase and gas-phase oxidation of graphitic carbon thin films including graphene layers were investigated, followed by synthesis of these thin films. Post-annealing of graphite on transition metal oxide substrates exhibited the removal of carbon located at the film/substrate interface as gaseous CO/CO_2. Irradiation of oxygen to the graphene surface was found to be a moderate oxidation process and formation of carbon-oxygen bond was confirmed. The oxidized graphene films showed the shaper D peak in Raman spectroscopy, suggesting that they contain a smaller variety of the oxygen-containing groups or defects compared with those prepared using the Hummers method.