Fabrication Method of Graphite Thin Films from Organic Solutions

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The saturated acetone: OrangeII solution was coated on SiO2 surface. Pure Ni metal was used as a catalyst that was deposited on the SiO2 before the OrangeII coating. The sample after annealing showed thin graphite layer formation. Raman spectroscopy measurements suggested that the OrangeII organic solution resolved on the Ni layer surface and formed graphite thin layers. Our results could provide an easy way to produce graphene sheet with low cost.

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Key words: graphite, graphene, crystal growth

1. INTRODUCTION
In recent years, atomically thin carbon film is one of the hottest materials in nanoelectronics. Graphite has been found for more than hundred years. However, it was believed that a single graphite sheet could not be produced in the isolated form. But in 2004, Novoselov and Geim, the Nobel Prize honors, and their collaborators achieved the single sheet formation of graphite [1]. This single layer graphite is called as graphene, and attracted a lot of attentions from many researchers. Graphene is mechanically strong, and has good flexibility, high thermal resistance and very high electron mobility at room temperature (RT). Some experimental results showed that the electron mobility of graphene was as high as 200,000 cm2V−1s−1 at RT when a sheet carrier density was about 1012 cm−2 [2-3]. However, the mobility was limited to 40,000 cm2V−1s−1 [2-3].

2. EXPERIMENTAL
Si (1 0 0) wafers were used as the starting materials. First, the Si (1 0 0) substrate was heated at a temperature of 1200 °C for 20 h in air by using a muffle furnace, which led to a 500 nm thick SiO2 layer growth on the Si. Next, pure Ni metal having thickness of 100 nm was deposited on the SiO2 in vacuum with a background pressure of 10−4 Pa. Finally, a saturated acetone: OrangeII (Acid Orange 7; C16H11N2NaO4S) solution was coated on the sample surface by dip-coating method. Afterword, the sample was annealed at 450 °C for 5 min in Ar atmosphere by an IR heater. A stylus surface profiler (Alfa-step 500) was used to check the height of OrangeII on the sample surface. The formation of graphite was investigated by microscopic Raman spectroscopy. Two Raman peaks were known for graphite materials, which were named D-band and G-band [8]. D-band originates from the disorder phase of graphite and appears at around 1350 cm−1 under laser excitation at an energy of 2.33 eV. G-band originates from vibration Raman mode and appears at around 1585 cm−1. An intense G-band indicates good crystallinity of graphite thin layer. The G / D intensity ratio is a factor of characterizing the graphite crystallization.

3. RESULTS AND DISCUSSION
Figure 1 (a) shows the surface morphology of a sample after OrangeII coating. The OrangeII was condensed to some areas. The average size of those areas was about 100-500 nm in diameter. The height of OrangeII was about 800 nm, which was determined by measuring the difference of Point 1 and Point 3 using the Alfa-step, as shown in Fig. 1 (a). After annealing, the OrangeII areas because thinner and was resolved to carbon, as shown in Fig. 1 (b). Raman spectra were measured for Point 1 to Point 8, and were shown in Fig. 1 (c) and (d),...
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Fig. 1. OrangeII deposited thin layer with a thickness of 800 nm on Ni/SiO\textsubscript{2} surface.
[a] Microscope image (x100) of the sample surface before annealing. [b] Microscope image (x100) of the sample surface after annealing. [c] Raman scattering spectra from Point 1 to 4 of Fig. 1 [a] on the sample surface before annealing. The intensities of spectra from Point 1 and 2 were divided by a factor of 100. [d] Raman scattering spectra from Point 5 to 8 of Fig. 1 [b] on the sample surface after annealing. The intensities of spectra from Point 5 and 6 were divided by a factor of 100.

respectively. Since Point 3, 4, 7, and 8 were the surface of SiO\textsubscript{2} and Ni, no significant Raman peak was observed for those points in the measuring wavenumber region. In contrast, clear Raman peaks were observed for Point 1, 2 and Point 5, 6. For Point 1, 2, which were for the sample before annealing, the Raman spectra showed broad backgrounds, suggesting a fluorescence from the functional groups connected on the anionic dyes. Figure 1 (d) shows the Raman scattering spectra from the annealed sample. Both Point 5 and 6 gave sharp Raman shift peaks at the wavelengths of D-band and G-band. The reduction of the background eliminated the partially resolving of OrangeII by the annealing, but the transition of benzene to graphite was not confirmed only by this spectra. The structure at 1240-1500 cm\textsuperscript{-1} arose from the hydrazone group in OrangeII. The peaks at around 1600 cm\textsuperscript{-1} corresponded to the C-C vibrations of benzene and naphthalene groups.
[9]. But the graphite formation should occur at the same time at the interface with Ni, which gave rise to the increase of the intensity at the position of D-band and G-band.

In Fig. 2, we changed the deposited OrangeII thickness. The height difference between Point 9 and 12 was 14 nm, suggesting an OrangeII layer having the same thickness, as shown in Fig. 2 (a). Fig. 2 (b) is the surface morphology of the sample after annealing. The black dots are condensed carbon. But even at the points 14 and 15, where were no significant black dots, the Raman spectra still indicated the formation of G-band and D-band, suggesting an existence of the graphite thin layer, as shown in Fig. 2 (d). Furthermore, making thin graphite from organic solutions was obtained by reducing the coated OrangeII thickness. So that a thinner organic layer deposited on the Ni/SiO2 surface should be the key point to get graphene-like graphite thin film.

It was not sure that the graphene formation was achieved only by Raman data in this work. We also could not measure the thickness of the very thin graphite layer. However, it is suggested that, some areas on the sample surface were graphene or several monolayers graphite from the Raman shift measurements.

In conclusion, we have deposited organic solution thin layers on Ni/SiO2 surface and obtained thin graphite areas by post annealing. Our process is easy and low cost, and may be useful for mass production of graphene sheets. Although our results were very preliminary, the easy and controllable process of producing graphene is highly expected. The authors would like to thank the support from the Green and Safety program of TUS.

References

(Received January 9, 2011; Accepted February 9, 2011)