# §16. Chemical Vapor Deposition of Graphene at a Low Temperature

Suda, Y. (Toyohashi Univ. Technol.),
Ichikawa, K. (Kobe City College of Technology),
Ashikawa, N.

Graphene is a planar material which is composed of the six-membered ring of carbon atoms in the shape of a sheet. The graphene specificities are high carrier mobility of 100 times higher than silicon, high transmittivity, and high mechanically flexibility. [1-3] Chemical vapor deposition (CVD) is one of the methods to synthesize graphene. $CH_4$ and $CH_3OH$ are commonly used as a source gas for graphene synthesis because they are safe gases. On the other hand, decomposition of $C_2H_2$ molecule is easy owing to the unsaturated hydrocarbon. Thus it is possible to synthesize graphene by using $C_2H_2$ gas at a lower temperature than by using $CH_4$ gas. In this study, we investigated the influence of $H_2$ concentration, the nickel film thickness and the cooling rate on the properties of graphene. The number of layers of the graphene and its domain size were evaluated by Raman spectroscopy and the surface of the graphene was observed using optical microscopy.

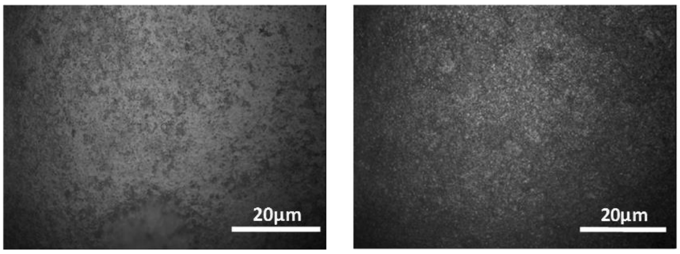
The CVD reactor and experimental procedure are detailed in our report. [4] After RCA cleaning of a thermally oxidized (100 nm thickness) Si wafer, a nickel layer with a thickness of 200-800 nm was deposited on the Si wafer by magnetron sputtering. In the CVD reactor, the nickel film was firstly annealed in $N_2/H_2$ gas mixture at 800 ºC. Then, $C_2H_2$ gas was added to the gas mixture for 5 min. After this step, the flow of $C_2H_2$ gas was cut off and the tube was rapidly cooled to 100 ºC for 10 min to 100 min while the gas flow of $N_2$ and $H_2$ gas mixture was continued at 450 sccm. The ratio of the flow rate of $H_2$ gas to that of $N_2$ gas was varied between 0 and 20 %, while the total gas flow rate was kept constant at 450 sccm.

First, influence of the nickel film thickness was investigated. All the nickel film thicknesses between 200 nm and 800 nm resulted in graphene synthesis. From the intensity ratio of the G band to the 2D band in the Raman spectra ($I_G/I_{2D}$), the number of layers of the synthesized graphene was evaluated. It was reported that $I_G/I_{2D}$ is strongly correlated with the graphene layers. $I_G/I_{2D} < 0.7$ for monolayer graphene, $0.7 < I_G/I_{2D} < 1.0$ for bilayer graphene and $1.0 < I_G/I_{2D}$ for multilayer graphene. [5] Therefore, in the cases of 400 nm and 600 nm, bilayer graphene was synthesized.

Next, the gas flow rate ratio of $H_2$ to $C_2H_2$ was changed from 0 to 20% while the gas flow rate of $C_2H_2$ was kept at 50 sccm, and that of $H_2/N_2$ gas mixture was kept at 450 sccm. As a result, monolayer graphene was synthesized at all the hydrogen ratios below 20%. This result suggests that the supply of too much hydrogen etched the graphene.

Then, the influence of hydrogen gas during the cooling in CVD process on the graphene property was investigated. We found that graphene with low defect density was synthesized when it cooled in pure nitrogen gas atmosphere. Also, the shortest cooling period of 11 min in this study resulted in the growth of monolayer graphene with high crystallinity and almost no defect.

An optical microscope image of the graphene samples with the cooling periods of 11 and 100 min is shown in Fig. 1. The dark region extended in the whole surface. This result indicates that the number of the graphene layers and density of defects increased with an increase of the cooling period due to too much carbon segregated from the nickel films as the cooling period increased.




(a) (b)

Fig. 1. Optical microscope images of graphene synthesized with different cooling periods: (a) 11 min and (b) 100 min.

Finally, the influence of the $H_2$ gas flow rate ratio during the cooling on the graphene property was again investigated. The gas flow rate ratio of $H_2$ to $H_2/N_2$ gas mixture was changed from 3% to 20%. It was found that an optimum $H_2$ gas flow ratio for the synthesis of a high quality monolayer graphene was 6% because of the largest $sp^2$ domain size and the smallest $I_D/I_G$.

In conclusion, we investigated the CVD conditions for synthesis of monolayer graphene by using acetylene gas on nickel catalytic substrate. We found that the optimal nickel film thickness was 800 nm. The amount of segregating carbon atoms from the nickel increased with a decrease of the nickel film thickness because the distance from the bottom of the nickel film to the surface decreased. An optimum $H_2$ concentration for the synthesis of monolayer graphene with high crystallinity was 6% because of the largest $sp^2$ domain size and the small amount of defects.

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3) Geimand, A. K. and Novoselov, K. S.: Nature Materials **6** (2007) 183.
4) Ichikawa, K. et al.: Journal of Materials Science and Engineering B **5** (2015) 341.
5) Kahng, Y. H. et al.: Nanotechnology **22** (2011) 045706.