Low-temperature graphene growth using epochal catalyst of PdCo alloy

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Palladium-Cobalt alloy as a catalyst was introduced to realize low temperature graphene growth on glass substrate by using remote RF plasma-enhanced chemical vapor deposition. Few layer graphene films were easily formed with high transmittance of 88.8% at temperature as low as 400°C, in good contrast with Ni catalyst in which no graphitic layer was formed at all at the same conditions. High decomposition rate of hydrocarbon gases and formation of nanosize aggregates giving rise to enhancement of carbon incorporation into PdCo alloy and consequently formation of graphene layers at such low temperatures are further discussed with observed Raman spectroscopy and x-ray diffraction. © 2011 American Institute of Physics. [doi:10.1063/1.3665616]

Graphene, an ideal 2D sheet of sp² hexagonal carbon structure, is a candidate for next-generation material in nanoscience and nanotechnology. In particular, several properties such as quantum transport, optical transmittance, superior mobility, and thermal conductivity have been studied for fundamental researches and various applications.1–5 Although the monolayer graphene was obtained by tapping for scientific purpose,6 large area graphene, which is required for numerous practical applications, has been available recently by several synthesis routes. Chemical vapor deposition (CVD) approaches using transition metal catalysts such as Ni and Cu have been demonstrated for producing large area monolayer and multilayer graphene, where hydrocarbon gases can be catalytically decomposed into carbons at high growth temperature of >900°C.3,7–11 It is generally believed that hydrocarbon gas can be decomposed catalytically on Ni surface and migrated into the Ni layer, followed by an out diffusion of carbon atoms to form graphene layers on Ni surface upon cooling.2 Dehydrogenation and liquid carbon-metal formation are critical steps for graphene growth, which require relatively high growth temperature. Thermal mismatch, the difference of thermal expansion coefficient between transition metal and graphene, is particularly large at high growth temperature, invoking wrinkles in graphene layers, which may act as scattering centers and could be an obstacle for high performance devices.

To overcome this limitation, several approaches with lower temperature have been established using methane gas with Cu and Al substrate under plasma CVD at low temperature (∼400°C).12 The produced graphene has poor quality in transmittance (∼80%) and sheet resistance (∼45 kΩ/sq) due to poor catalytic carbon decomposition rate at low temperature. Because of this, solid Poly(methyl methacrylate) (PMMA) or liquid benzene precursors on Cu substrate have been introduced as a carbon source and annealed further at low temperature (∼400°C).13 However, it is difficult to control the number of graphene layers due to presumable thermal evaporation of carbon materials. The issue with CVD approach, which is advantageous in controlling several parameters for controlling number of graphene layers and quality of graphene layer, is the poor catalytic decomposition rate of hydrocarbon gases and inefficient carbon dissolution in catalyst at low growth temperature. Therefore, development of a new catalyst which can enhance catalytic decomposition rate of hydrocarbon gas and maintaining liquid metal is necessary for low temperature graphene growth. Until now, modification of catalyst structure for the purpose of low temperature graphene growth has not been explored.

Pd-based alloy has been commonly used as a cathode in fuel cell. The superior catalytic reaction of Pd and secondary metals (Co, Ni, Cr) alloy has been known to be more efficient than pure Pd in reducing oxide surface on the cathode due to the reduction of the density of states (DOS) in d-electron at the Fermi level.14,15 Furthermore, the dehydrogenating capability of PdCo catalyst has been investigated at atmospheric pressure at low temperature (300–500°C).16 Although the melting temperature of PdCo alloy is not reduced much, the melting temperature of graphite/PdCo alloy is expected to be low to form liquid metal state at low growth temperature. Here, we report low temperature synthesis of graphene layers using PdCo alloy as a catalytic layer which can be activated at low temperature (∼400°C) with radio frequency plasma-enhanced chemical vapor deposition (RF PECVD). A few graphene layers (4~5 layers) with a transmittance of 88% was synthesized directly on slide glass substrate. Detailed studies on the structural modifications of PdCo alloy with various growth temperatures were further discussed.

Co composition of 4.5% in PdCo alloy (Pd:Co = 22:1) was used in our study because lower Co composition is more advantageous for lowering growth temperature.16 Ni catalyst of 300 nm in thickness on SiO2 (300 nm)/Si substrate was also used for comparison. Synthesis of graphene was carried out in a PECVD. Two samples were simultaneously preheated up to 400, 500, and 600°C with 100 sccm H2 gas feeding for 10 min for reducing catalyst. The gas mixture (C2H4:H2 = 5:45 sccm) was then flown into the chamber for 5 min under a RF plasma power of 250 W. PECVD is more advantageous than thermal CVD in decomposing hydrocarbon sources at
The furnace was cooled down to room temperature and the synthesized graphene layer from PdCo alloy was transferred onto 300 nm of SiO$_2$/Si wafer by wet etching process as reported in the previous paper. Slide glass was also used directly to demonstrate low temperature synthesis. Crystal quality of graphene films was analyzed by confocal Raman spectroscopy (CRM-200, Vitec, Germany), atomic force microscopy (AFM) (5500AFM, N9410S, Agilent Technologies, USA), and electrical properties by a four-point probe method (Model 2000 6-1/2-Digit DMM, Keithley Instruments Inc., USA). X-ray diffraction (XRD) (D8 FOCUS 2.2KW, Bruker AXS, Germany) and high-resolution transmission electron microscopy (HR-TEM) (JEM-2100F, Jeol, Japan) were also used for further analysis of PdCo alloy.

Figures 1(a) and 1(b) show Raman spectra of the synthesized graphene film on (a) 100 nm PdCo film and (b) 300 nm Ni film on SiO$_2$ substrate at different temperatures. Figure 2(a) is the TEM image of PdCo catalyst which was heat-treated at 400 °C in the absence of hydrocarbon gases, while maintaining identical graphene growth conditions. The surface was corrugated but no compositional segregation was found in energy dispersive x-ray spectroscopy (EDX) analysis. Figure 2(b) shows optical image of the transferred graphene on 300 nm SiO$_2$/Si substrate. The synthesized graphene film was uniform over 1 × 1 cm$^2$. The synthesized graphene film has been transferred onto TEM grid, as shown in Fig. 2(c), again demonstrating the planar structure of the film. This is in good contrast with graphene synthesized on Ni even at temperature of 600 °C, where the graphene flakes were formed locally.

To understand the catalyst role of PdCo alloy at low temperature, we investigated structural alteration of PdCo alloy at various temperatures by using XRD measurements. In the case of PdCo from Figs. 3(a) and 3(b), every lattice was shifted to low angle as the temperature decreased. This is in good contrast with Ni case in Figs. 3(c) and 3(d), in which no appreciable peak shift was observed. The lattice parameters of PdCo(111) direction in both samples were extracted and shown in Fig. 3(e). The lattice parameter of PdCo alloy at room temperature was 3.88 Å, larger than 3.83 Å of Pd$_2$Co alloy. This value increased to a maximum value of 3.93 Å at 400 °C and decreased further as the temperature increased. On the other hand, the change of the lattice parameter of Ni(111) direction was almost negligible. Since hydrocarbon gases were flown simultaneously as the temperature increased, some carbon atoms may be associated within catalytic metals and carbon source at different temperature ranges. Once the hydrocarbon source is adsorbed onto the catalyst surface, the hydrocarbon gases can be decomposed into carbon by dehydrogenation. While PdCo is more efficient for dehydrogenation at lower temperature below 500 °C, Ni is more effective at high temperature. We found that in the case of PdCo, D/G ratio increased further at 700 °C and G' band disappeared and no graphene layer was formed at higher temperature (data not shown here).

Figure 2(a) is the TEM image of PdCo catalyst which was heat-treated at 400 °C in the absence of hydrocarbon gases, while maintaining identical graphene growth conditions. The surface was corrugated but no compositional segregation was found in energy dispersive x-ray spectroscopy (EDX) analysis. Figure 2(b) shows optical image of the transferred graphene on 300 nm SiO$_2$/Si substrate. The synthesized graphene film was uniform over 1 × 1 cm$^2$. The synthesized graphene film has been transferred onto TEM grid, as shown in Fig. 2(c), again demonstrating the planar structure of the film. This is in good contrast with graphene synthesized on Ni even at temperature of 600 °C, where the graphene flakes were formed locally.
size of particles (or aggregates) was evaluated by using Scherrer’s equation where the full width at half maximum was obtained from (111) peak. The size of PdCo alloy particles at room temperature was 2.45 nm, much smaller than 4 nm of Ni particles. This size of PdCo alloy particles increased rapidly up to 2.96 Å at 400 °C and was saturated to 3.62 Å at 500 °C, still smaller than Ni sizes, whereas the size of Ni particles was not altered much from its value (3.9 Å) at room temperature. This again supports low melting temperature of PdCo alloy. The carbon incorporation into PdCo was particularly higher at 400 °C, which was confirmed from the depth profile by secondary ion mass spectroscopy (not shown here).

As a demonstration of low temperature graphene synthesis, a slide glass of sizes (2.5 × 7.5 cm²) was directly used to synthesize graphene layer, as shown in Fig. 4(a). Once the graphene was formed, PdCo was directly etched away by FeCl₃ etchant without transfer. Similar D/G intensity ratio of graphene was formed, PdCo was directly etched away by FeCl₃ etchant without transfer. The synthesized graphene layer on slide glass at 400 °C shows uniform transmission of 88.8% at a sheet resistance of 66 kΩ/sq. The quality of the graphene film can be further improved by optimizing Co composition and CVD growth conditions. Our work opens a route to directly grown graphene at low temperature for semiconductor devices.