Controlled synthesis of bilayer graphene on nickel

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Abstract

We report a uniform and low-defect synthesis of bilayer graphene on evaporated polycrystalline nickel films. We used atmospheric pressure chemical vapor deposition with ultra-fast substrate cooling after exposure to methane at 1,000°C. The optimized process parameters, i.e., growth time, annealing profile and flow rates of various gases, are reported. By using Raman spectroscopy mapping, the ratio of 2D to G peak intensities ($I_{2D}/I_G$) is in the range of 0.9 to 1.6 over 96% of the 200 μm × 200 μm area. Moreover, the average ratio of D to G peak intensities ($I_D/I_G$) is about 0.1.

Keywords: Bilayer graphene, Chemical vapor deposition, Raman spectroscopy

Background

Graphene, a monolayer of sp$^2$-hybridized C atoms arranged in a honeycomb structure, has attracted a lot of attention due to its excellent electrical, mechanical and optical properties [1-3]. Monolayer and bilayer graphene (BLG) are semi-metals with zero band gap. The intrinsic band gap has been the key in semiconducting devices. Band gap can be induced by patterning graphene into nano-ribbons [4-10]. Another method to introduce band gap is to apply electric field in the stacking direction of BLG [11-14].

Graphene synthesis on transition metals by chemical vapor deposition (CVD) or via segregation of solid carbon sources is generally a scalable process [15-24]. Transition metals such as Ni, Cu, Pt, Ir and Pd have been used as substrates for graphene growth [25-29]. Several hydrocarbons, like methane (CH$_4$), acetylene, ethylene, propane, etc., have been used in atmospheric and low-pressure CVD as a carbon source [25]. Besides the CVD of the above mentioned gases, C$_{60}$ and solid polymers such as poly(methyl metha-crylate), polystyrene and acrylonitrile butadiene styrene have also been decomposed to grow graphene [30-32].

Graphene synthesizes on Ni due to segregation of carbon at high temperatures. Due to the high solubility of carbon in Ni, precipitation of extra carbon occurs at the metal surfaces during cooling. Since the precipitation is a non-equilibrium process, this makes thickness control of graphene a challenge [33,34]. The segregation of extra carbon during the cooling process can be decreased by reducing Ni film thickness. Moreover, extra carbon segregation can also be controlled by controlling the cooling rate [15,22,35-37]. Very high cooling rate has been reported to deposit amorphous carbon deposition, whereas low cooling rate leads to no growth [15]. It has been reported that the carbon segregation on Ni is non-uniform at low temperatures. However, CH$_4$ has high decomposition temperature, which helps in constant carbon coverage over the Ni surfaces [38]. Furthermore, high melting point of Ni enables high-temperature annealing, which results in larger domains, thus making it favorable for large-area low-defect growth [25].

In this paper, we report a method to control the precipitation of extra carbon on Ni surface during the cooling-down process. We reduce the sample temperature from the growth temperature of 1,000°C to room temperature in a few seconds, which leads to a uniform BLG growth.

Methods

BLG was grown on a 300 nm Ni film, evaporated on SiO$_2$ (300 nm)/Si substrate. SiO$_2$/Si substrate was treated with acetone (10 min), methanol (10 min), deionized (DI) water rinse (10 min) and nanostrip (20 min; commercial Piranha substitute), followed by another DI water rinse (10 min). After cleaning, Ni was evaporated by using an e-beam evaporator at 1Å/s. Ni/SiO$_2$/Si

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samples were gently cleaned in UV ozone for 2 min before loading in the CVD furnace. UV ozone eliminates organic contaminants from the Ni film, which is important for uniform growth. Process gases were supplied by Airgas (Denver, CO, USA) with research grade 5.0 (minimum purity 99.999%). The samples were loaded into the CVD furnace (1-inch tube diameter; Lindbergh/Blue, Thermo Scientific, Logan, UT, USA) at room temperature and heated to 700°C in 200 sccm Ar ambient. At 700°C, 65 sccm H2 was introduced in addition to Ar, and the samples were annealed for another 10 min. The temperature was ramped to 1,000°C in Ar/H2 ambient. To stabilize the growth temperature, the samples were further annealed for 10 min after reaching 1,000°C. Ar/H2 annealing sequence leads to increased grain size and decreased surface roughness [18,22]. Finally, H2 was turned off, and BLG was synthesized by introducing CH4 into the furnace in addition to the already flowing Ar gas. A wide process parameter space was explored, which includes (a) varying the growth time (50, 60 and 120 s) under a constant CH4 flow rate (23 sccm) and (b) varying the flow rates (6, 12 and 23 sccm) under a constant growth time (120 s). After the growth, the sample temperature was reduced to room temperature within a few seconds by pulling the quartz tube out of the hot region of the furnace.

For material characterization, micro-Raman spectroscopy (Raman Nicolet Almega XR Spectrometer, Thermo Scientific) was used in the point scan and the area scan mode [3,39,40]. A 532 nm laser (10 mW power) was used with a 0.6 μm spot size, 15 s scan time and four scans per point. To examine the uniformity of the synthesized graphene, the ratio of 2D to G peak intensities (I2D/I_G) ratio) was taken over 20 locations for the samples grown under 23 sccm of CH4 for 120 s, 60, and 50 s. The I2D/I_G ratio is close to unity with these varying growth times. This quenching method inhibits the precipitation of extra C on the Ni surface and thus controls the number of layers and the uniformity of the graphene for various growth times. Furthermore, after turning the CH4 off, if there is some residual C inside the furnace, the ultra-fast cooling suppresses its further segregation. Moreover, the effect of the CH4 flow rate was also studied for constant growth time. Figure 2b shows the Raman spectra of samples for which the growth time was 120 s with CH4 flow rates of 6, 12 and 23 sccm. It shows that the BLG growth is consistent for a wide range of flow rates.

Another important observation is that the intensity of the D peak decreases as the growth time increases from 50 to 120 s, as shown in Figure 2a. The ratio of D to G peak intensities (I_D/I_G) was taken over 20 locations for the samples grown under 23 sccm of CH4 for 50, 60 and 120 s. The mean and standard deviation of I_D/I_G ratio are plotted in the error bar graph shown in Figure 3. The average I_D/I_G ratio for the sample grown under 23 sccm of CH4 for 120 s is 0.1 with a standard deviation of 0.05, which suggests a low defect density of BLG for these parameters. Moreover, Figure 3 also shows that the average defect density decreases with the increasing growth time. Figure 2b also shows that the defect density of BLG is small for the samples grown under wide CH4 flow rates for 120 s.

We find that quenching the samples from the hot region of the furnace helps in reducing the non-equilibrium precipitation of extra carbon on the Ni surfaces during the cooling process, and that the main growth mechanism is diffusion of carbon on Ni surface due to the decomposed CH4. With fast cooling, the reduced sample temperature stops further segregation of carbon due to any residual carbon inside the furnace, even after CH4 flow was turned off. The thickness of the graphene is almost constant even with a wide range of CH4 flow rates (6 to 23 sccm), which shows that the segregation process is rather self-limiting. Furthermore, the growth temperature is high due to high decomposition temperature of CH4 that supports the uniform carbon diffusion over the Ni surface. This helps in growing uniform BLG with less defect density. Moreover, as the growth time is decreased, the average intensity of the D peak increases, which indicates incomplete growth. This further verifies the self-limiting equilibrium segregation of carbon on Ni surface, with reduced out-diffused carbon atoms from the C-Ni solution due to fast cooling. To verify the proposed growth mechanism, graphene was grown on 300 nm Ni film, with 23 sccm CH4 flow rate for 120 s, cooling the samples within the furnace. Due to slow cooling, the precipitation of carbon on Ni surface from the C-Ni solution is a dominant process.

Yet, another way to reduce the precipitation of extra carbon is to reduce the thickness of Ni film as less thick.
films would absorb less carbon and thus contribute to further decrease in out-diffused carbon. To characterize this effect, the growth was performed on 200 and 100 nm thick Ni films, with 23 sccm CH$_4$ flow rate for 120 s. For the 200 nm Ni film, the $I_{2D}/I_G$ ratio is close to unity, and the area uniformity is similar to the 300 nm thick films. However, growth on 100 nm Ni film results in increased surface roughness. Although the $I_{2D}/I_G$ ratio

![Figure 1](image1.png) **Figure 1** Two-dimensional Raman intensity map for bilayer graphene. (a) $I_{2D}/I_G$ ratio (ratio of 2D to G peak intensities). (b) $I_{2D}$ (intensity of 2D peak). (c) $I_G$ (intensity of G peak). (d), (e) and (f) show $I_{2D}/I_G$, $I_{2D}$ and $I_G$ respectively, for a different area. BLG was grown by using CVD on 300-nm of evaporated Ni film under CH$_4$/Ar (23:200 sccm) at 1,000°C for 120 s. The total area of each view map is 200 μm × 200 μm.

![Figure 2](image2.png) **Figure 2** Raman spectra for various growth conditions. (a) Increasing the growth time decreases the D peak intensity for 23 sccm of CH$_4$. (b) BLG quality is uniform over wide CH$_4$ flow rates for 120-s growth time.
is still around unity in this process, surface coverage is only 50%.

Conclusions

In conclusion, we have reported a method to synthesize bilayer graphene through CVD of CH₄ on polycrystalline Ni films with an ultra-fast cooling technique. The number of graphene layers is uniform over a wide area with low defect density. The growth is consistent over a certain variation of CH₄ flow rate and growth time.

Competing interests

Both authors declare that they have no competing interests.

Authors’ contribution

HR and AU have equal contribution to this work and the manuscript. Both authors read and approved the final manuscript.

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