Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling

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Paper inside paper

Large-Area Synthesis of High-Quality and Uniform Graphene Films On Copper Foils

Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R. D.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S.

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Experimental steps:

I. Growth of graphene on Cu in a hot wall furnace consisting of a 22-mm ID fused silica

tube heated in a split tube furnace

- II. Removal of Cu substrate
- III. Transfer of free graphene to other surface

I. Growth:

- (1) Loading of the the fused silica tube with the Cu foil, evacuate, back filling with hydrogen, heating to 1000°C and maintaining a $H_2(g)$ pressure of 40 mTorr under a 2 sccm flow;
- (2) Stabilization of the Cu film at the desired temperatures, up to 1000°C, and introduction of 35 sccm of $CH_4(g)$ for a desired period of time at a total pressure of 500 mTorr;
- (3) Cooling of the furnace to room temperature after exposure to CH₄.

II. Removal of Cu substrate

- **by etching** in an aqueous solution of iron nitrate
- III. Transfer:

Coating of the surface of the graphene-on-Cu with polydimethylsiloxane (PDMS) or poly-methyl methacrylate (PMMA) and lifting up of the PDMSgraphene from solution after dissolution of Cu.



Figure S1. Time dependence of experimental parameters: temperature, pressure, and gas composition/flow rate.

Ref.:Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R. D.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. *Science* **2009**, *324*, 1312.



Figure S2. Photos of as-received Cu foil, and Cu foil covered with graphene. The Cu foil with graphene has a smooth surface and is "shinier" compared to the as-received Cu foil, which has a thin but rough oxide layer.

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Figure S3. SEM images of graphene on Cu with different growth times of (A) 1 min, (B) 2.5 min, (C) 10 min, and (D) 60 min, respectively.

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Fig. 1. (A) SEM image of graphene on a copper foil with a growth time of 30 min. (B) High-resolution SEM image showing a Cu grain boundary and steps, two- and three-layer graphene flakes, and graphene wrinkles. Inset in (B) shows TEM images of folded graphene edges. 1L, one layer; 2L, two layers. (C and D) Graphene films transferred onto a SiO₂/Si substrate and a glass plate, respectively.

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Fig. 2. (A) SEM image of graphene transferred on SiO₂/Si (285-nm-thick oxide layer) showing wrinkles, as well as two- and three-layer regions. (B) Optical microscope image of the same regions as in (A). (C) Raman spectra from the marked spots with corresponding colored circles or arrows showing the presence of one, two, and three layers of graphene. (D to F) Raman maps of the D (1300 to 1400 cm⁻¹), G (1560 to 1620 cm⁻¹), and 2D (2660 to 2700 cm⁻¹) bands, respectively (WITec alpha300, laser = 532 nm, ~500-nm spot size, 100× objector). Scale bars, 5 µm. Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R. D.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. *Science* **2009**, *324*, 1312.

Conclusion from

Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R. D.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. *Science* **2009**, *324*, 1312:

***Low solubility of C in Cu: Cu is an excellent candidate for making large-area graphene films with uniform thickness *** The graphene growth is somehow surface mediated and self-limiting

This work follows the above one:

Use of isotopic labeling of the carbon precursor to study the mechanism and kinetics of CVD growth of graphene on Ni and Cu substrates.

Logic behind this work:

Difference in the 12C and 13C Raman modes

Monitoring of the spatial distribution of graphene domains

Not a new logic:

Monitoring the growth of carbon nanotubes by carbon isotope labelling Fan, S.; Liu, L.; Liu, M. *Nanetechnology* **2003**, *14*, 1118–1123.

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Important notes:

A. Experimental:

1. Use of Ni and Cu as graphene substrates: Why?

Graphene obtained on SiC single crystals: good mobility, but may be limited to devices on SiC only, since transfer to other substrates such as SiO₂/Si has not been demonstrated yet and might be difficult. There are reports on the growth of graphene on metal substrates such as Ni, Co, Ru, Ir, Cu, etc.,: By UHV-chemical vapor deposition (CVD) or "normal" CVD.

Cost, grain size, etchability, and wide use and acceptance by the semiconductor industry: Ni and Cu

2. Use of thin Ni film (~700 nm, deposited by sputtering on SiO₂/Si wafer) rather than on Ni foil:

To minimize the saturation time and the amount of carbon in the Ni film since

the solubility of C in Ni is high, about \sim 0.9 at. % at 900 \sim C.

- 3. Use of Cu foil having a thickness of 25 μ m in case of Cu: Because the carbon solubility in Cu is negligible.
- 4. Sequential dosing: Introduction of both normal methane and ${}^{13}CH_4$ (99.95% pure) to the growth chamber in a specific sequence.
- 5. Expression for the duration of exposure of methane:

 $^{j}t_{i}$ as, where j = 12 or 13 denotes $^{12}CH_{4}$ or $^{13}CH_{4}$,

and *i* denotes the step in the sequence (e.g., ${}^{13}t_1$ means the first gas introduced was ${}^{13}CH_4$ with the duration of exposure being t_1).

Input on mechanism:

Studies on the formation of carbon films by cooling Ni foils saturated with C at high temperatures.

Shelton, J. C.; Patil, H. R.; Blakely, J. M. *Surf. Sci.* **1974**, *43*, 493–520;Isett, L. C.; Blakely, J. M. *Surf. Sci.* **1976**, *58* (2), 397–414; Eizenberg, M.; Blakely, J. M. *Surf. Sci.* **1979**, *82* (1), 228–236; Eizenberg, M.; Blakely, J. M. *J. Chem. Phys.* **1979**, *71* (8), 3467–3477.

Findings: A monolayer graphite grows first by C segregation, followed by more C precipitation thus forming graphite.

Use of Blakely's explanation by the authors of this work: To explain CVD growth of FLG films on Ni film

Suggestion: The graphene growth is somehow surface mediated and self-limiting



Figure 1. Schematic diagrams of the possible distribution of C isotopes in graphene films based on different growth mechanisms for sequential input of C isotopes. (a) Graphene with randomly mixed isotopes such as might occur from surface segregation and/or precipitation. (b) Graphene with separated isotopes such as might occur by surface adsorption.

Case I: Substrate where C is highly soluble: In the case of metals like Ni where the carbon solubility is high, carbon diffuses into the metal first before segregating and precipitating to the surface Result: Sequential dosing (not losing) of ${}^{12}CH_4$ and ${}^{13}CH_4$ is expected to yield a uniform C-metal solution, and the segregated and/or precipitated graphene will consist of randomly mixed isotopes.

Case 2: Substrate where C is less soluble: No diffusion of C into the metal, graphene grown with the sequential dosing of ${}^{12}CH_4$ and ${}^{13}CH_4$ grows by surface adsorption and the isotope distribution in the local graphene regions will reflect the dosing sequence employed (Figure 1b).

Figure 3: Results of graphene grown on Ni sheet:



Figure 2. Optical micrograph and distribution of C isotopes in a FLG film grown on Ni. (a) An optical micrograph of a FLG film transferred onto a SiO₂/Si wafer. (b) The corresponding Raman map of location of the G bands and (c) a typical Raman spectrum from this film, showing the film consists of randomly mixed isotopes (with an overall composition of ~45% ¹³C and ~55% ¹²C). Scale bars are 5 μ m.

---The variation of color contrast: Non-uniformity in thickness; consists of one to tens of graphene layers

---Uniformity of the G-band and uniform shift \rightarrow Uniform isotopic distribution across the metal surface ----> growth happens by segregation followed by precipitation

Figure 3: Results of graphene grown on Cu foils:



Figure 3. Micro-Raman characterization of the isotope-labeled Graphene grown on Cu foil and transferred onto a SiO_2/Si wafer.

Figure 3: Results of graphene grown on Cu foils:



Figure 3. (a) An optical micrograph of the identical region analyzed with micro-Raman spectroscopy.
(b) Raman spectra from ¹²C-graphene (green), ¹³Cgraphene (blue), and the junction of ¹²C- and ¹³C-graphene (red), respectively, marked with the corresponded colored circles in (a) and (e).
(c) Line scan of the dashed lines in (d-f). Scale bars are 5 μm.

Uniform G band: Uniformity of transferred graphene Existence of D band : Presence of defects Color contrast of the optical micrograph + Raman spectra: SLG

Line scan of graphene on Cu



Figure 3c shows a line scan (marked with dashed lines across Figures 3(d-f) where the ¹²C-graphene and ¹³C-graphene domains are clearly seen with the blue line representing the G¹³ (i.e., ¹³C-graphene) domains and the pink line representing the G¹² (i.e., ¹²C-graphene) domains. The green line, which is the most uniform across the film, is the overall G band intensity (G¹³ + G¹²) with the peak corresponding to the wrinkle in the film. Scale bars are 5 μ m.

Time evolution of graphene growth on Cu:



cm⁻¹). Scale bars are 5 μ m.

Optical micrograph (Figure 3a) + and the Raman maps (Figures 3d-i):

----Uniform **intensity** distribution-- \rightarrow the thickness is uniform except for the wrinkles (bright lines)

----No overlap of the graphene layers where the domains join--- \rightarrow there is crystallographic registration to the Cu substrate.

***If there were overlap, a high contrast or bright line would be present in the micrograph and the G-band Raman maps.

---Sequential distribution of 13C and 12C -- \rightarrow graphene growth on Cu is based on the surface adsorption mechanism.

The D maps



Figure 3. Integrated intensity Raman maps of (g) $D^{13+12}(1275-1375 \text{ cm}^{-1})$, (h) $D^{13}(1275-1325 \text{ cm}^{-1})$, and (i) $D^{12}(1325-1375 \text{ cm}^{-1})$ of the area shown in (a). Scale bars are 5 μ m.

Possible mechanism of defect formation:

Different T_c of graphene and Cu or Roughness of Cu surfaces----> formation of pentagonal and/or heptagonal arrangements of carbon atoms ----> defects---> crystallographic registration of C to the Cu substrate----> no overlap of graphene layers where the domains join---> absence of high contrast or bright line

Low defect boundaries (indicated by the white arrows in Figure 3g)--- \rightarrow "Good" registration between two domains

Presence of small fraction of few layer flakes



Figure 4. Raman imaging spectroscopy of few-layer (FL) regions. (a) Optical micrograph. (b-d) Raman maps of overall G, G¹³, and G¹², respectively, corresponding to the region in (a). The FL regions can be easily located from the optical micrograph due to their high contrast (a) and also from their high intensity in the overall G map (b). The layer and growth sequences are schematically shown in (e), where red, orange, yellow show ¹³C grown in the first minute, blue, purple, teal show ¹²C grown in the second minute, and maroon, lime show ¹³C grown in the third minute. Scale bar is 2 μm.

----Consist of separated 13C and 12C rings--- \rightarrow Growth by surface adsorption, but not by segregation/precipitation.

----Show the same or smaller number of isotopic sequential rings as the first layer graphene-- \rightarrow flake growth stops once the Cu surface is fully covered with graphene.

----Termination of flake growth due to the full coverage of Cu surface with graphene $--\rightarrow$ the carbon source for flake growth is from the catalytic decomposition of methane by the active Cu surface.

Study of growth rate:

The edge growth rate

----First graphene layer: :for the first minute=3-6 μ m/min :for the second minute =1-2 μ m/min

---- Filling of Cu surface area by domains--- \rightarrow decrease in the number of catalytic sites- \rightarrow decrease in domain advancement rate

-----Second and third layers(~160 and ~40 nm/min, respectively) ----- lower concentration of Cu catalyst available to promote the decomposition of methane in the regions of 2^{nd} and 3^{rd} layer growth----> multilayer flakes occupy a very small area (~5%) of the whole film.

-----Growth of graphene only during the first three dosings (total 8 dosings): The fourth and subsequent doses played no role because the surface was already saturated with graphene.

-----Growth occurs in two-dimensions and thus is a consequence of a surface-adsorption process

---Growth is selflimiting since there is no catalyst to promote decomposition and growth after the first layer of carbon (graphene) is deposited

The Last Slide

According to author:

-----Study of defects---flake defects, interdomain defects

-----Investigation of the reason of decrease of domain advancement rate with time

-----Transport physics of discrete regions of isotopically labeled graphene

-----Study of device possibility of discrete regions of isotopically labeled graphene

Reader's hunch

Thanks!

Materials and Methods

Growth and transfer of graphene films

Graphene films were primarily grown on 25-µm thick Cu foils (Alfa Aesar, item No. 13382, cut into 1 cm strips) in a hot wall furnace consisting of a 22-mm ID fused silica tube heated in a split tube furnace; several runs were also done with 12.5- and 50-µm thick Cu foils (also from Aesar). A typical growth process flow is: (1) load the fused silica tube with the Cu foil, evacuate, back fill with hydrogen, heat to 1000°C and maintain a $H_2(g)$ pressure of 40 mTorr under a 2 sccm flow; (2) stabilize the Cu film at the desired temperatures, up to 1000°C, and introduce 35 sccm of $CH_4(g)$ for a desired period of time at a total pressure of 500 mTorr; (3) after exposure to CH_4 , the furnace was cooled to room temperature. The experimental parameters (temperature profile, gas composition/flow rates, and system pressure) are shown in Fig. S1. The cooling rate was varied from > 300°C/min to about 40°C/min which resulted in films with no discernable differences. Fig. S2 shows the Cu foil with the graphene film, compared to the as received Cu foil.

Graphene films were removed from the Cu foils **by etching** in an aqueous solution of iron nitrate. The **etching time** was found to be a function of the **etchant concentration**, the **area**, and **thickness** of the Cu foils. Typically, a 1 cm² by 25-µm thick Cu foil can be dissolved by a 0.05 g/ml iron nitrate solution over night. Since **graphene grows on both sides of the Cu foil**, two films are exfoliated during the etching process. We used **two methods to transfer** the graphene from the Cu foils: (1) after the copper film is dissolved, a substrate is brought into contact with the graphene film and it is 'pulled' from the solution; (2) the surface of the graphene-on-Cu is coated with polydimethylsiloxane (PDMS) or polymethyl methacrylate (PMMA) and after the Cu is dissolved the PDMSgraphene is lifted from the solution, similar to the method reported in the reference mentioned in the main text. The first method is simple, but the graphene films break and tear more readily. The graphene films are easily transferred with the second method to other desired substrates such as SiO₂/Si, with significantly fewer holes or cracks (< 5% of the film area).



