Transfer-free synthesis of multilayer graphene on silicon nitride using reusable gallium catalyst

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ABSTRACT
Direct growth of graphene film on dielectric substrates is significant for the applications in electronic devices, which can avoid additional complicated and damaging treatments. Despite the advances, a facile way is urgently required to prepare graphene directly on insulators at a low temperature. We presented a gallium (Ga)-assisted atmosphere chemical vapor deposition to synthesize graphene films on silicon nitride (Si3N4). Liquid Ga was dropped on the substrate as a catalyst and flowed away after growth, achieving graphene on Si3N4 (100 nm)/SiO2 (100 nm)/Si and recovering the most of Ga. Multilayer graphene film was formed at the interface between Ga and the substrate. The growth of graphene was investigated by regulating the growth conditions, and an interfacial precipitation mechanism was proposed. Graphene synthesized with recovered Ga droplet is comparable to that prepared using pure Ga, revealing the reusability of Ga catalysts.

1. Introduction
Graphene, a two-dimensional material with π-π conjugated structures, has exhibited great potential to promote the development of material science [1]. The excellent electronic [2], optical [3], thermal [4], and mechanical [5] properties make graphene an ideal candidate material for broad applications in electronics and optoelectronics etc. Multiple methods have been developed to produce graphene, such as mechanical exfoliation [1], epitaxial growth on SiC [6], chemical reduction of exfoliated graphite oxide [7], and chemical vapor deposition (CVD) [8]. In particular, CVD shows promising advantages in the synthesis of high-quality graphene with high controllability and productivity. To date, continuous graphene films and single crystal graphene with a size up to centimeters have been produced on metals [9–13], making a significant step for the industrial production of graphene. However, as most of electronic devices are fabricated on dielectric substrates, transfer processes are required for the graphene grown on metals, which can introduce damages and contaminations. Consequently, direct growth of graphene on dielectric substrates exhibits remarkable predominance in high-performance electronic applications.

During the past years, different strategies were demonstrated to prepare graphene on insulators by using traditional thermal CVD, such as metal-free growth [14–16] and metal assisted methods [17–28]. Metal-free process is a way that can completely avoid metallic residues on the grown graphene. Up to now, both high-quality graphene crystals and films have been synthesized on various dielectric substrates. Due to the lack of metal catalysts, very high growth temperatures (> 1100 °C) are commonly required to accelerate the decomposition of carbon sources to grow graphene, leading to high energy consumption. As an alternative way, sublimed metal vapors and deposited metal layers can be introduced to promote the growth of graphene on dielectric substrates. Metal vapors, such as Cu [23–26], Ni [27,28], Ga [19,20], can not only improve the growth rate, but also avoid metal contaminations. But the growth temperatures are still as high as 1050 °C, and the quality of the as-grown graphene needs further improvements. Another method

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is to deposit a metal layer on the target substrate, followed by a low-
temperature annealing process for graphene growth. The carbon
sources are dissociated into carbon species which further assemble into
graphene at the interface between the metal layer and dielectric sub-
strate. The capped metal layer will be removed after growth to obtain
graphene on the insulator. By designing the carbon source and metal
layer, graphene films were synthesized on dielectrics at temperatures
below 500 °C [29]. However, additional deposition and post-removal of
metals are required, which will consume lots of energy and catalyt.

Liquid Ga has been used as catalyst to prepare graphene for several
years, exhibiting excellent catalytic ability [19,20]. Here, we demon-
strated a facile way to synthesize multilayer graphene on Si₃N₄
(100 nm)/SiO₂ (100 nm)/Si with Ga droplets at temperature as low as
800 °C. As a room-temperature liquid metal (melting point: 30 °C), Ga
possesses unique advantages in graphene growth. Unlike Cu and Ni
layers which need to be deposited via electron-beam evaporation, Ga
can be directly dropped on the substrate and is readily to flow away
after growth, achieving the recovery of Ga. The multilayer graphene
film was directly formed at the interface between the substrate and Ga,
indicating a precipitation growth process. Raman spectrometer, scan-
ning electron microscope (SEM), and transmission electron microscopy
(TEM) were used to reveal the morphology and structure of the as-
grown graphene. The uniformity and quality of graphene grown with
recovered Ga were characterized to confirm the reusability of Ga cat-
ylist. The electronic property of the graphene film was evaluated by
fabricating field-effect transistors (FETs), exhibiting mobilities of
101–166 cm² V⁻¹ s⁻¹.

2. Experimental

2.1. CVD growth of graphene

The Si₃N₄/SiO₂/Si substrates (Si₃N₄: SiO₂ = 100:100 nm), which were cut into pieces of 10 × 10 mm², were cleaned using acetone,
isopropl alcohol and deionized water for 10 min in an ultrasonic bath,
then dried with pure nitrogen gas. A substrate was firstly loaded in a
quartz boat, and liquid Ga was dropped on the surface of the substrate.
The interfacial growth process was carried out in a traditional atmo-
sphere pressure CVD system. The quartz boat containing Ga droplet and
Si₃N₄/SiO₂/Si was located at the center of a quartz tube. After the air in
the system was ejected by a hydrogen flow of 200 sccm, the furnace was
heated to 800 °C in 28 min. The liquid carbon source was introduced by
a bubbling method. Using a simple bubbling device, the H₂ flow was
introduced to the bottom of the liquid, generating bubbles and carrying
methanol vapors away through the outlet pipe. The precursor was
brought into the system by H₂ flow to start growth. After growth, the
methanol was cut off and the quartz tube was rotated (about 15–25°)
and shaken slightly to make the Ga droplet flow away. At last, the
furnace was shut down and pull to the downstream to cool down.
The obtained graphene grown on the substrate was immersed in a dilute
hydrochloric acid to remove the residual Ga. Syringes were used to
recover the internal Ga catalyst for next growth cycle of graphene.

2.2. Graphene characterization

The optical images were obtained by optical microscopy (Olympus
DP27). The morphologies of the as-grown graphene on Si₃N₄/SiO₂/Si
were directly characterized by SEM (Hitachi S-4800, 15 kV). The
equipped energy dispersive spectrometer (EDS) was used to perform
elementary analysis of selected area. A Raman spectrometer (LabRAM
HR Evolution with laser excitation at 532 nm) was used to evaluate the
quality and uniformity of graphene. The surface elemental analysis was
performed on an ESCALAB 250Xi spectrometer equipped with Al K α X-
rays as the excitation source. High-resolution TEM (HRTEM) images of
graphene were achieved on a JEOL JEM-2100F microscope operating at
200 kV. The selected area electron diffraction (SAED) pattern of
graphene was achieved as well.

2.3. FET measurements

Electrical properties of the graphene were evaluated by fabricating
FETs. The bottom–gate FETs were fabricated with a "lift-off" process.
Electrodes were firstly patterned into a PMMA layer with an electron
beam lithography system (JBX-6300FS). Then Ti/Au (2/30 nm) was
deposited in the thermal evaporation system. The channel length (L)
and width (W) were measured to be 600 nm and 1 μm, respectively. To
obtain a better contact, the devices were thermally annealed at 200 °C
under H₂/Ar (10/90 sccm) atmosphere for 20 min. Electrical charac-
teristics of the FETs were performed in air at room temperature
using a semiconductor analyzer (Keithley 4200–SCS) with a Lakeshore
probe station. The hole mobility was calculated according to the
equation: μ = (∆V₉₀/∆V₉₀/Vₐ₉₀, Cₛₛ, Cₚₚ) (2.32 × 10⁻¹² F m⁻²) is the
gate capacitance of Si₃N₄(100 nm)/SiO₂(100 nm), and Vₐ₉₀ was set to be
−0.1 V.

3. Results and discussion

Si₃N₄/SiO₂/Si substrates, in which silicon nitride is a suitable bar-
rier to inhibit the diffusion of gallium [30], were used in this work. Ga
have been used to catalyze the dissociation of CH₄, C₂H₄, and C₂H₂ in
previous reports [31,32]. To achieve low temperature growth of gra-
phene, methanol, with lower bond energy of C-H (401 kJ/mol) [33],
was used as the carbon source. The growth process of graphene using
reusable Ga is depicted in Fig. 1. A substrate was located in a quartz
boat, and Ga liquid was dropped on it. Then the synthesis of graphene
was performed using an atmosphere CVD system at 800 °C which is
much lower than those of metal-free and metal-vapor assisted processes
[14,15,23–26]. After 2-h growth, a graphene film was formed at the
circular interface between Si₃N₄/SiO₂/Si and the Ga droplet. Subse-
quently, when the boat was sloped by rotating the whole tube, the Ga
droplet flowed off the substrate under gravity, while the graphene film
was attached to the Si₃N₄/SiO₂/Si, realizing the separation of Ga (Fig.
S1b). Previously, Fu et al. placed a target substrate on the graphene
grown on liquid Ga, and then introduced a horizontal force to overcome
the Ga-Ga adhesion [34]. During the horizontal movement of gra-
phene/substrate, the graphene was separated from liquid Ga and at-
tached to the target substrate, achieving a sliding transfer of graphene.
Here, compared with transferred graphene, the directly grown gra-
phene can be intimately contacted with the substrate during the
thermal growth process, leading to stronger interfacial adhesion [35].
This interaction can enable graphene to be closely attached to the
substrate and overcome the force between graphene and Ga. In addi-
tion, at 800 °C, Ga shows good fluidity and poor wettability (Fig. S1a)
to graphite (the contact angle is 130°) [36], facilitating the separation
of graphene and Ga. Eventually, the graphene film was onto the substrate,
and the Ga droplet was recovered. The trace of residual Ga can be easily
removed by dilute hydrochloric acid [37]. The optical image of the top
surface of Ga and related Raman spectrum (Fig. S2) indicate that
multilayer graphene was also formed on the surface of the Ga droplet.
But no graphene was attached to the bare area (Fig. S1b) during the
rolling of Ga, which is attributable to the inadequate contact between
the substrate and the graphene grown on Ga. It should be noted that
excessive leaning of the tube can lead to fast rolling of Ga during which
part of the multilayer graphene may be ripped away, leading to circular
and streak holes on the film (Fig. S3). The recovered Ga droplet was
used for subsequent synthesis of graphene.

The crystallinity and uniformity of graphene were characterized by
X-ray photoelectron spectroscopy (XPS) and Raman spectrometer. The
C₁s XPS curve (Fig. 2a) was resolved into three peaks, corresponding to
sp² carbon (284.7 eV), sp³ carbon (285.3 eV) in the defects, and oxygen
groups (287.1 eV), respectively. As shown in the survey scan and Ga 2d
spectrum (Fig. 2b), Ga was not detected, indicating that the graphene

was metal-free. The quality and layer number of graphene (800 °C, 2 h) were evaluated by using Raman spectroscopy. Typical bands of graphene were selected in the Raman spectrum (Fig. 2c): D (1347 cm \(^{-1}\)), G (1580 cm \(^{-1}\)), and 2D (2692 cm \(^{-1}\)). The D peak is originated from the defects and edges of graphene. The intensity ratio of D band to G band was about 0.6, indicating the quality is comparable to that of graphene synthesized with Cu vapor catalysts [23,26]. The full width at half-maximum of the 2D peak was about 57.5 cm \(^{-1}\), which is in accordance with that of multilayer graphene [38,39]. Fig. 2d–f shows the Raman mappings of the intensity and position of 2D band (\(I_{2D}\) and \(P_{2D}\)), and the intensity ratio of the 2D band to G band (\(I_{2D}/I_G\)), which suggests the acceptable uniformity of graphene film in terms of the overall scale. As shown in Fig. 2e, the positions of the 2D peaks (\(P_{2D}\)) in the range of 2692–2697 cm \(^{-1}\) are about 15 cm \(^{-1}\) higher than that of mechanical exfoliated graphene on SiO\(_2\)/Si [40]. This significant upshift of the 2D band can be attributed to the strong interaction between graphene and the substrate, which was caused by the high growth temperature [40,41]. Fig. 2f shows that the \(I_{2D}/I_G\) is in the range of 0.65–0.75, implying the multilayer structure of the as-grown graphene film [41,42].

The contrast of the SEM image is related to the graphene layer

![Fig. 1. Illustration of graphene growth on Si\(_3\)N\(_4\)/SiO\(_2\)/Si using reusable Ga catalyst.](image)

![Fig. 2. XPS and Raman characterizations of the as-grown graphene films. (a–b) C1s (a) and survey scan (b) curves. (c) Raman spectrum. (d–e) Raman mappings of \(I_{2D}\) (d), \(P_{2D}\) (e), and \(I_{2D}/I_G\) (f). Scale bars in (d–f) are 100 \(\mu\)m.](image)
numbers and can be exploited to evaluate the homogeneity of graphene [3,43]. The low-magnification SEM (Fig. 3a) and optical (Fig. S1c) images reveal the morphology of graphene grown on Si$_3$N$_4$/SiO$_2$/Si macroscopically. At the micro-scale, the high-magnification SEM image in Fig. 3b shows that the graphene film consists of plenty of nano-sized graphene domains, indicating lots of boundaries and defects. Besides, the dark area reveals that the graphene is few layer [44,45], in agreement with the Raman spectrum (Fig. 2c). Fig. 3c shows the intensity profile of $I_{2D}/I_G$ along the blue arrow in Fig. 3a. The graphene signals were only extracted from the circular area which was covered with the Ga droplet, indicating that the graphene was grown at the interface between the substrate and Ga. The edge of the graphene film was characterized by selected area elemental analysis (Fig. S4). No Ga signal was observed from both graphene area and the bare substrate, indicating the absence of graphene in the external area. The Raman mappings (Fig. S5) also showed the clear border of graphene, which was in accordance with EDS analysis. These characterizations identified that the growth of graphene was limited to the interfacial area between Ga and the substrate. As no graphene was formed in the other area, Ga vapors showed negligible promotion of graphene growth on metals: surface catalyzed growth on metals with low catalytic activity of Ga vapor for graphene growth, which is determined by the vapor pressure. The pressure of Ga vapors at 800 °C is about two orders of magnitude lower than that at 1050 °C in previous works [19,20,46]. Moreover, the lower vapor pressure is helpful to reduce the deposition of Ga on the bare substrate. The HRTEM image (Fig. 3d) shows the edge of graphene film. The measured layer-to-layer spacing (about 0.34 nm) is in line with graphitic interlayer spacing [47], revealing that the graphene film is about 2–3 layers. The corresponding SAED pattern (Fig. S6) confirms the polycrystalline structure of graphene [48–50].

Two types of mechanisms have been proposed to explain the graphene growth on metals: surface catalyzed growth on metals with low solubility of carbon and precipitation method using high carbon-soluble metals [51]. In surface catalyzed process, graphene can only be grown on the exposed surface of metal catalyst. As for the precipitation approach, the carbon atoms, which are pre-deposited or dissociated from carbon sources, can be diffused into the metal and precipitate on both sides of the metal layer as graphene films. Ga has been used to synthesize graphene via both surface-catalyzed and precipitation approaches [22,37,52]. In this work, considering that graphene was formed at the interface of the substrate and Ga droplet, the growth of graphene was attributed to the precipitation process (Fig. 4a), in coincidence with previous works [22,52]. CVD growth of graphene can be divided into two major stages: the decomposition of the carbon source and the formation of graphene by the attachment of the dissociated carbon species. Ga has excellent catalytic ability for the dissociation of the C–H bonds [22,37,52]. On the surface of droplet, the precursor can be decomposed into carbon atoms which are dissolved into Ga. During the growth, the carbon atoms migrated to the interface and precipitated as graphene films. Fig. S7a shows the Raman spectra of graphene grown after 4 h at different temperatures. With the increasing temperature, the intensity of 2D band becomes sharper, implying the improvement of the graphene quality. Higher temperature could offer sufficient energy for the decomposition of methanol, improving the crystallinity of graphene [53]. When the growth temperature was further elevated, the deposition of Ga vapors was enhanced, resulting in more Ga residues. The Raman spectra of graphene grown under different H$_2$ flows were extracted to investigate the influence of H$_2$ (Fig. S7b). When the flow rate of H$_2$ is as low as 50 sccm, low-quality graphene was obtained. With the increasing H$_2$ flow, the 2D band shows growing intensity, indicating the improvement of graphene crystallinity. Increasing H$_2$ will restrain the dehydrogenation of precursors [53], preventing the fast generation of carbon species. The gently decomposition of methanol was proposed to avoid the fast assembly of the carbon species at the interface, leading to the improvement of crystallinity. The time dependent evolution of the graphene was described in the Raman spectra (Fig. 4b). When the growth time was 30 min, only nanographene was obtained (black line) [54].
prolonging the growth time to 1 h, the crystallinity of graphene was improved, which can be ascribed to the interfacial graphitization of Ga [55]. After 2-h growth, multilayer graphene film was produced. When the growth time was 4 h, the layer number of graphene continued to increase (Fig. 4b red curve), indicating the continuous carbon migration and graphene growth. By optimizing the growth parameter, graphene film obtained after 2-h growth (Figs. 2 and 3) showed best quality and uniformity. Similar to the growth process on Ni, it is hard to obtain uniform single-layer graphene due to the carbon segregation growth process which is difficult to control. Besides, the growth time is longer than that of graphene grown on the surface of Ga at higher temperatures (> 1000 °C). This is resulted from the lower rate of precursor decomposition and carbon diffusion at 800 °C. It has been demonstrated that the quality and layers of the graphene synthesized on Ni are affected by the cooling process. Because of the high solubility of carbon in Ni, the dissolved carbon atoms can precipitate during the cooling stage, influencing the as-prepared graphene. Here, the influence of the cooling rate on graphene was investigated as well. Fig. S8 depicts the Raman spectra of graphene grown for 4 h through different cooling processes: natural and fast (push the furnace away) cooling, showing little difference in quality and layer numbers. In addition, the recovered Ga was dropped on a fresh substrate and annealed at 800 °C for hours without carbon sources. After cooling to the room temperature, no graphene was obtained on the substrate, indicating that no carbon precipitated from the recovered Ga. As gallium-carbon is an insoluble system, it is difficult for trace dissolved carbon to separate out during the cooling process, leading to negligible effect on the graphene film. This feature also makes it achievable to reuse the Ga catalyst for repeated growth of graphene. As shown in the Cls XPS curve, no carbide was formed during the growth.

We used a syringe to retrieve the inside Ga of the whole droplet, avoiding the external Ga layer covered with graphene. Because when the Ga was directly used, the covered graphene may be stuck to the fresh substrate during the high temperature process, which may affect the uniformity of new-grown graphene film. The Ga catalyst was used for five times to prove its reusability. Fig. 4b shows the Raman spectra of the graphene prepared using repeatable Ga. There is no significant difference in quality and layer numbers between the graphene synthesized with reused and pure Ga. Fig. S9 shows the I_D/I_G maps of the graphene synthesized using Ga catalyst after 2–5 times growth. It is apparently that all graphene films have acceptable uniformity, exhibiting high feasibility to reuse the Ga catalyst.

The electronic properties of the graphene synthesized on Si_3N_4/SiO_2/Si after 2-h growth were measured by fabricating back-gated FETs. Fig. 5 shows the transfer and output characters of the prepared FET device in air. In the transfer curve (Fig. 5a), the FETs shows obvious p-doping effect in air. This can be attributed to the doping effect of the substrate and the absorption of p-type doped molecules (H_2O, O_2) from air [56–58], in coincidence with previous work [59]. After the measurement of 20 devices at room temperature, the calculated hole mobilities were in the range of 101–166 cm^2 V^{-1} s^{-1} (average value is about 125.3 cm^2 V^{-1} s^{-1}). This result is inferior to those of graphene grown on metals, which is attributed to the defects in graphene films.

4. Conclusions

We demonstrated a facile way to directly synthesize graphene on Si_3N_4/SiO_2/Si using recoverable Ga catalysts. The quality and uniformity of as-grown graphene film was characterized by using Raman spectroscopy, SEM, and TEM. The growth mechanism was investigated by regulating the growth parameters, and an interfacial precipitation process of carbon was presented. Profiting from the liquid phase and good fluidity, the Ga droplet can be introduced and recovered conveniently. The properties of graphene films synthesized using recovered
Ga are comparable to those of graphene grown with fresh catalysts, exhibiting the reusability of Ga droplets. The as-grown graphene films were directly used to fabricate FET devices. This work could open a novel approach to synthesize graphene on insulators for electronic devices.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.diamond.2018.11.009.

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