Chemical Vapor Deposition Synthesis and Raman Spectroscopic Characterization of Large-Area Graphene Sheets

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ABSTRACT: We present a chemical vapor deposition (CVD) method to catalytically synthesize large-area, transferless, single- to few-layer graphene sheets using hexamethyldisilazane (HMDS) on a SiO2/Si substrate as a carbon source and thermally evaporated alternating Ni/Cu/Ni layers as a catalyst. The as-synthesized graphene films were characterized by Raman spectroscopic imaging to identify single- to few-layer sheets. This HMDS-derived graphene layer is continuous over the entire growth substrate, and single- to trilayer mixed sheets can be up to 30 μm in the lateral dimension. With the synthetic CVD method proposed here, graphene can be grown into tailored shapes directly on a SiO2/Si surface through vapor priming of HMDS onto predefined photolithographic patterns. The transparent and conductive HMDS-derived graphene exhibits its potential for widespread electronic and opto-electronic applications.

1. INTRODUCTION

Since its first discovery in 2004, graphene has generated enormous research interest owing to its extraordinary electrical and physical properties.1,2 To date, graphene films have been employed in many applications, such as field-effect transistors,3−7 chemical sensors,8−10 biological sensors and devices,11−13 and transparent electrodes.14−16 For all of these applications, uniform and large-area synthesized graphene films on an insulating substrate with predefined lithographic patterns are highly desirable. Among the several methods of preparing graphene, chemical vapor deposition (CVD) is the most promising approach for the growth of large-area, transparent, conducting graphene films. In CVD reactions, various types of metal catalysts, such as copper (Cu),17 nickel (Ni),18 Ni/Cu alloy,19 and ruthenium (Ru),20 as well as gas- and solid-phase carbon precursors (e.g., methane16 and polymer films21), have been carefully selected to mediate the growth mechanisms of synthesized graphene films. The major difference between these growth mechanisms stems from the distinctive solubilities of carbon in different metallic catalysts during the CVD reactions. However, despite the success of synthesizing large-area graphene with these CVD methods, the prepared graphene must be separated from the growth substrate following reaction by transferring it to a receiving silicon (Si) wafer for further electronic fabrication. For this reason, developing efficient transfer techniques is important; for instance, the deposition of a gold (Au) thin film on the top of the graphene grown on Cu foils could facilitate a successful transfer of the as-synthesized graphene to a silica substrate.22 However, some of these transfer methods may introduce contamination and likely defects to the graphene surface; thus, it is detrimental to maintaining the pristine properties of graphene. Therefore, it is imperative that transferless techniques for large-area graphene films in CVD reactions be developed for subsequent device fabrication.

Bilayer graphene films can be formed between the catalytic Ni layer and the insulating SiO2/Si substrate by spin-coating polymer films, such as poly-(methyl methacrylate) (PMMA), on the top of a Ni layer precoated on a Si wafer (i.e., SiO2/Si substrate), which results in the diffusion of carbon atoms from the top to the bottom of the Ni layer during the CVD reaction.23 Similarly, by sandwiching a carbon precursor between a catalytic Ni film and a supporting Si wafer, carbon can diffuse into the Ni layer to eventually form graphene on both sides of the Ni layer under appropriate annealing conditions.24 In addition to the Ni catalyst, large-area graphene films synthesized via the transferless method can also be obtained using a Cu catalyst in the CVD reaction; graphene films formed at the interface of a Si wafer and a precoated Cu thin film have been previously reported.25 Furthermore, using floating Cu and hydrogen atoms as catalysts in gas-phase reaction for the decomposition of hydrocarbons (CH4 or CHx radicals) also allows the direct graphitization of carbon radicals on oxide surfaces.26

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In this article, we propose another new transferless approach to catalytically synthesize large-area graphene films on a SiO$_2$ (300 nm thick)/Si substrate via a CVD reaction using hexamethyldisilazane (HMDS) as a reaction precursor for the carbon source. HMDS is a convenient material in conventional device fabrication and has been widely used to increase the adhesion between photoresists and hydrophilic SiO$_2$ surfaces (i.e., a Si wafer) in a standard lithographic process. First, we modified HMDS on the SiO$_2$/Si surface through vapor priming HMDS on a Si wafer, which converted the hydrophilic SiO$_2$ surface into a hydrophobic surface by replacing the hydroxyl end groups with methyl groups. Then, alternating Ni/Cu/Ni layers were sequentially thermo-evaporated onto the HMDS-modified SiO$_2$/Si wafer to act as catalysts in the CVD reaction. During the synthetic reaction at elevated temperature in a low-pressure CVD (LPCVD) process, carbon from HMDS diffused into the Ni–Cu alloy because of the melting of the Ni/Cu/Ni layers. After the reaction, a fast cooling and annealing process was implemented to yield single- to few-layer HMDS-derived graphene at the interface of the Ni–Cu alloy and SiO$_2$/Si surface. By removing the top layer of Ni–Cu alloy with FeCl$_3$ etchant, the HMDS-derived graphene films grown on the entire Si wafer are ready for subsequent device fabrication without any further transfer. Next, we characterized the HMDS-derived graphene films by micro-Raman spectroscopic imaging and vibrational analysis; the surface topography of the synthesized graphene was examined via atomic force microscopy (AFM). The advantage of using HMDS as a reaction precursor to synthesize graphene in this work is that HMDS can be modified on an arbitrarily designed photoresist pattern on a Si wafer with a tailored shape. Therefore, using HMDS as a carbon source to synthesize graphene films is well suited for widespread electronic and opto-electronic applications.

2. EXPERIMENTAL SECTION

2.1. Preparation of Graphene Sheets. A flowchart for the growth of graphene in the catalytically assisted CVD reaction used in this work is illustrated in Figure 1; each procedure is discussed below.

2.1.1. Modification of HMDS. A Si wafer with 300 nm thick thermally grown oxide was first sonicated in acetone and then in isopropyl alcohol. Subsequently, the surface of the SiO$_2$/Si substrate was treated with oxygen plasma at 100 W for 5 min to remove residual organic material. To modify the HMDS (Aldrich, reagent grade, >99%) on the SiO$_2$/Si substrate, the Si wafer was suspended in a well-cleaned flask prior to the addition of 0.5 mL of HMDS. The wafer was suspended in a well-cleaned flask prior to the addition of 0.5 mL of HMDS. The wafer was immersed into a well-cleaned flask prior to the addition of 0.5 mL of HMDS. The wafer was immersed into a well-cleaned flask to dissolve and vaporize HMDS on a Si wafer to act as catalysts in the CVD reaction. The sample substrate was then loaded into a furnace in an Ar/H$_2$ mixture (total pressure of 0.4 Torr) for reaction at 1050 °C for 2.5 min. After CVD reaction, the sample substrate was rapidly removed from the hot zone of the furnace with the aid of a magnet rod. (c) At this point, the metal catalysts had formed a Ni–Cu alloy; the sample substrate was then cooled to room temperature at a cooling rate of 35 °C/min. (d) Finally, the sample substrate was immersed into 1 M FeCl$_3$ etchant to dissolve the metallic alloy and yield the as-grown HMDS-derived graphene on the SiO$_2$/Si substrate.

![Figure 1. Flowchart for the catalytically assisted growth of HMDS-derived graphene sheets in a CVD reaction.](image)

Figure 1. Flowchart for the catalytically assisted growth of HMDS-derived graphene sheets in a CVD reaction. (a) A monolayer of HMDS was modified on a SiO$_2$/Si substrate prior to the thermal evaporation of metallic catalysts. (b) Alternating Ni/Cu/Ni layers were deposited sequentially on the HMDS-modified substrate as catalysts in the CVD reaction. The sample substrate was then loaded into a furnace in an Ar/H$_2$ mixture (total pressure of 0.4 Torr) for reaction at 1050 °C for 2.5 min. After CVD reaction, the sample substrate was rapidly removed from the hot zone of the furnace with the aid of a magnet rod. (c) At this point, the metal catalysts had formed a Ni–Cu alloy; the sample substrate was then cooled to room temperature at a cooling rate of 35 °C/min. (d) Finally, the sample substrate was immersed into 1 M FeCl$_3$ etchant to dissolve the metallic alloy and yield the as-grown HMDS-derived graphene on the SiO$_2$/Si substrate.
on the HMDS-derived graphene surface. Finally, the sample substrate was blow-dried with N₂ gas.

2.2. AFM Topographic Mapping. Surface topographs of the HMDS-derived graphene were obtained with an AFM (Digital Instruments, Bioscope S2) combined with an inverted optical microscope (Nikon, TE2000-U). The AFM was placed on an antivibration table and housed in a soundproof cage to eliminate vibrational and acoustic noise, respectively. For AFM measurements, a patch (40 × 40 μm²) of the HMDS-derived graphene was scanned in a tapping mode with 256 scan lines and 512 line samples at a scanning rate of 0.25 Hz, a resonant frequency of 267.5 kHz, and an amplitude set point of 0.63 V, which was close to the target amplitude of 0.74 V.

2.3. Micro-Optical Imaging. Micro-optical images of the HMDS-derived graphene were obtained using an optical microscope (Olympus, BX 51) equipped with a 100× objective and a charge-coupled device (CCD) camera (Sony, KMS-1259AI-S).

2.4. Micro-Raman Spectroscopic Mapping. The vibrational modes of the HMDS-derived graphene were characterized by micro-Raman spectroscopic imaging conducted in a commercial Raman spectrometer (NT-MDT, NTEGRA). A He–Ne laser at λ = 633 nm was used as the excitation source. The laser beam was focused by a 100× objective onto the HMDS-derived graphene sample with a focused spot of ~1 μm². The laser output power was set to ~250 μW to avoid laser-induced heating damage to the graphene sheets. Raman scattering signals at 1250–2800 cm⁻¹ were collected by a CCD camera (Andor Technology, DV401) that was integrated into the NTEGRA spectral system. The characteristic peak of the Si substrate at 520.7 cm⁻¹ was used as a calibration reference for the measured wavenumbers. Raman mapping data were obtained by scanning a selected area of the sample surface with a step size of 0.5 μm and an exposure time of 2 s at each point. Typically, the number of points for a scanned area of 32 × 32 μm² was preset to 64 × 64; therefore, the step size was 0.5 μm.

2.5. Electrical Measurement. The current (I_SD) vs source-drain voltage (V_SD) was measured with a picoammeter (Keithley, 6487) by scanning V_SD from −40 to +40 mV, which was applied to the HMDS-derived graphene device via e-beam-evaporated Cr (5 nm)/Au (45 nm) conducting electroplates.

3. RESULTS AND DISCUSSION

3.1. Graphene Synthesis Reaction. The carbon feedstock is one of the most important factors for the successful synthesis of graphene in CVD reactions. As shown in Figure 1a, HMDS was selected as a carbon source to be vapor primed onto a SiO₂/Si substrate prior to the CVD reaction in which alternating Ni/Cu/Ni layers (depicted in Figure 1b) were employed as metal catalysts. Initially during the CVD reaction, the inner Ni layer functioned as a carbon sink, accepting the carbonaceous fragments pyrolyzed from HMDS at temperatures ≥900 °C. At 900–1050 °C, the Cu atoms in the middle Cu layer diffused into both the inner Ni layer (i.e., the carbon sources). Finally, the sample substrate was blow-dried with N₂ gas.
sink layer) and the outer Ni layer (i.e., the protection layer), consequently forming a Ni−Cu alloy layer as illustrated in Figure 1c. At this point, the carbon solubility in the Ni−Cu alloy is lower than that of the inner Ni layer; as a result, the saturated Ni−Cu alloy tends to reject carbons at the interface of the Ni−Cu alloy and SiO₂ surface, which results in the formation of large-area graphene films directly on the SiO₂/Si substrate. By removing the reacted Ni−Cu alloy with FeCl₃ etchant, the as-grown HMDS-derived graphene sheets directly adhere to the SiO₂/Si substrate (Figure 1d) without the necessity of further transfer for subsequent device fabrication.

3.2. Micro-Optical and AFM Characterizations. Figure 2a shows a micro-optical image of an obtained wafer-scale HMDS-derived graphene. The coverage area of the as-grown HMDS-derived graphene sheets depends only on the size of the Si wafer used in the CVD reaction. Single- to few-layer graphene sheets were synthesized from a sample of HMDS-modified SiO₂/Si substrate covered with alternating catalytic layers of Ni (150 nm)/Cu (100 nm)/Ni (150 nm). The sample underwent a CVD reaction under 0.4 Torr of Ar (40 sccm) and H₂ (2 sccm) at 1050 °C for 2 min. After reaction, the sample substrate was rapidly removed from the hot zone in the furnace. The sample was then held at the same ambient condition as during the reaction (0.4 Torr, 40 sccm Ar, and 2 sccm H₂), while it cooled down to 25 °C at an average cooling rate of 35 °C/min. The surface topography of the HMDS-derived graphene scanned by AFM, as shown in Figure 2b, exhibits a roughness of ∼2.5 nm due to a small amount of FeCl₃ etchant remaining on the graphene surface and to a vacancy without graphene. The vacancy on the as-synthesized graphene can be suppressed with the longer reaction time of modifying HMDS on SiO₂/Si surface, assuring that each silanol group on the SiO₂ surface has a complete reaction with the trimethylsilyl groups (−Si(CH₃)₃) of HMDS, i.e., the well formation of trimethylsilox groups (−O−Si(CH₃)₃) on the SiO₂ surface. A well HMDS modification can increase the coverage rate of the as-grown graphene. Contrarily, small holes could be formed in the as-grown graphene sheets resulting from the incomplete HMDS modification. The number of layers of graphene sheets can be determined by Raman analysis from the intensity ratio of
2D- to G-bands (represented by \( I_{2D}/I_G \)) and the full width at half-maximum (FWHM) of the 2D spectral line shape (referred to as FWHM\(_{2D} \)). In general, \( I_{2D}/I_G \) and FWHM\(_{2D} \) for CVD-based graphene are, respectively, \( \geq 2 \) and \( \sim 45 \text{ cm}^{-1} \) for single-layer, \( \sim 1 \) and \( \sim 60 \text{ cm}^{-1} \) for bilayer, and \( < 0.5 \) and \( \sim 80 \text{ cm}^{-1} \) for trilayer sheets. Accordingly, the number of layers of graphene sheets (Figure 2c) was characterized by Raman spectroscopy (Figure 2d) with excitation at \( \lambda = 633 \text{ nm} \). The \( I_{2D}/I_G \) and FWHM\(_{2D} \) of regions I (2.12 and 45 cm\(^{-1} \)), II (1.18 and 52 cm\(^{-1} \)), III (0.68 and 75 cm\(^{-1} \)), and IV (0.32 and 94 cm\(^{-1} \)) characterize the graphene as single-, bi-, tri-, and few-layer sheets, respectively.

### 3.3. Micro-Raman Spectroscopic Mapping

The distribution of layers and the structural quality of the HMDS-derived graphene sheets were characterized by micro-Raman spectroscopic mapping. We first selected region I (8 \( \times \) 8 \( \mu \text{m}^2 \)) in Figure 3a for micro-Raman mapping analysis for which the measured \( I_{2D}/I_G \) and \( I_{2D}/I_G \) are presented in Figure 3b,c, respectively. From spectroscopic analysis, it can be seen that a large proportion of region I possesses \( I_{2D}/I_G \approx 1 \) (histogram listed in Figure 3d) and FWHM\(_{2D} \approx 50 \text{ cm}^{-1} \), indicating that this local region is mainly composed of bilayer graphene sheets. As shown in Figure 3b, there are areas with \( I_{2D}/I_G < 0.3 \) in region I, suggesting that small defects exist in the graphene structure. As shown in Figure 3e, the area of region II (32 \( \times \) 32 \( \mu \text{m}^2 \)) marked in Figure 3a is composed of bilayer and trilayer mixed graphene sheets. Figure 3f summarizes the structural distribution of region II: \( \sim 35\% \) bilayer and \( \sim 45\% \) trilayer; the remaining 20\% consists of few-layer graphene sheets.

### 3.4. Effect of Reaction Parameters

The reaction parameters of hydrogen flow rate, reaction time, and rapid cooling rate in the CVD reaction are crucial for the structural quality of synthesized graphene sheets. To determine the optimal growth conditions, samples of an HMDS-modified SiO\(_2\)/Si substrate covered with the same catalytic layers of Ni (75 nm, inner)/Cu (100 nm, middle)/Ni (225 nm, outer) were used under various reaction parameters.

#### 3.4.1. Hydrogen Flow Rate

Samples were loaded into a furnace at 1050 \( ^\circ \text{C} \) under a total pressure of 0.4 Torr with a fixed Ar flow rate of 40 sccm and various hydrogen flow rates of 1, 2, and 3 sccm. After CVD reaction, the as-grown graphene films were characterized by Raman spectroscopy, and the results are shown in Figure 4a. Analysis of the measured \( I_{2D}/I_G \) and FWHM\(_{2D} \) (as indicated in the Raman spectra) indicates that the synthesized graphene appeared as few-layer sheets at \( \sim 1 \text{ sccm} \) but became thinner at 2 sccm. However, excessive hydrogen could overconsume the carbon source in the reaction, resulting in a deficit of carbon at the interface of Ni–Cu alloy and SiO\(_2\)/Si wafer. As a consequence, structural defects occurred in the graphene synthesized with a hydrogen flow rate of 3 sccm as indicated by the increase of the D-band at \( \sim 1350 \text{ cm}^{-1} \) in Figure 4a.

#### 3.4.2. CVD Reaction Time

The structural quality of the as-grown graphene sheets also depends on the selection of an appropriate CVD reaction time. To determine the effect of
reaction time, HMDS-modified SiO₂/Si substrates were prepared under the same experimental conditions as those of Figure 4a with the hydrogen flow rate fixed at 2 sccm. The Raman spectra in Figure 4b indicate that a prolonged reaction time promotes graphene growth. Few-layer graphene sheets started to grow when the reaction lasted for 2 min. When a longer reaction time of 2.5 min was used, bilayer and trilayer graphene films became dominant. Beyond 2.5 min, the structural quality of the as-grown graphene sheets degraded because the Ni–Cu alloy became saturated with carbon moieties and tended to reject additional carbon; this effect resulted in an increase in the number of layers of graphene sheets and the onset of aggregation of amorphous carbon fragments.

3.4.3. Rapid Cooling Rate. At the end of the CVD reaction used for graphene synthesis, the sample was rapidly removed from the hot zone and placed in a cold area in the furnace for annealing. A fast cooling rate is important for the growth of HMDS-derived graphene. To determine the optimal cooling rate, samples were prepared with a total pressure of 0.4 Torr and flowing Ar (40 sccm) and H₂ (2 sccm) at 1050 °C for 2.5 min. We compared two cooling rates, 35 °C/min and 25 °C/min, as shown in Figure 4c. While a cooling rate of 35 °C/min is better for growth of bi- and trilayer mixed graphene sheets, a slower cooling rate of 25 °C/min results in the formation of few-layer sheets. Figure 4c shows the Raman analysis of a randomly chosen area (100 × 100 μm², divided by 64 × 64 points) of synthesized graphene in which bi- and trilayer sheets cover more than 50% of the newly formed area at 35 °C/min cooling; this coverage decreases to 20% when the cooling rate is 25 °C/min during annealing. This decrease can be explained by the fact that more carbon could be extracted from the Cu–Ni alloy during a longer precipitation period with slower annealing, thus increasing the number of layers of graphene sheets and resulting in few-layer sheets. At 25 °C/min cooling, only 20% of the growth area is covered by bi- and trilayer sheets, but 40% is covered by few-layer graphene sheets.

3.4.4. Catalytic Ni-Layer Thickness. The thickness (75, 150, and 225 nm) of the inner Ni catalytic layer was also examined as a function of the reaction temperature under optimal growth conditions for large-area graphene sheets. These tests were performed under a mixture of Ar (40 sccm) and H₂ (2 sccm) in the CVD reaction for 2.5 min (total pressure of 0.4 Torr) with a reaction temperature of 900 to 1050 °C, which increased stepwise by 50 °C. Following the reaction, an area of 100 × 100 μm² (divided by 64 × 64 points) was used for Raman analysis. As demonstrated in Figure 4d, the 150 nm thick inner Ni layer helps to improve the coverage ratio (from 28% to 50%) of graphene sheets that are less than three layers thick as the reaction temperature increases from 900 to 1050 °C. Using a 75 nm thick inner Ni layer, few-layer graphene sheets grew due to the higher proportion of Cu in the Ni–Cu alloy, which consequently increased the carbon rejection rate in the reaction. In comparison, a thicker (225 nm) inner Ni layer not only decreases the coverage ratio of graphene sheets (i.e., forming vacancies without graphene) but also produces structural defects. The uneven distributed, defective graphene sheets were the result of a lower proportion of Cu in the catalytic Ni–Cu alloy, which lead to increased solubility of carbon during the reaction, decreased carbon rejection during annealing, and, consequently, reduced crystallinity in the as-grown graphene.

In the CVD synthesis of large-area graphene sheets, some processes could be considered to improve the quality of the as-synthesized graphene. In the step of cleaning the HMDS-modified SiO₂/Si substrate, in spite of multiple sonications in acetone and isopropl alcohol to remove unreacted HMDS following the surface modification, physically adsorbed residual HMDS might still remain on the SiO₂/Si surface, leading to inhomogeneous supply of carbon source at the interface of the alternating Ni/Cu/Ni layers and SiO₂/Si surface. By properly increasing the sonication power and longer sonication time, the uniformity of the as-grown graphene sheets can be improved. In addition, the thickness of the inner Ni layer determines not only the percent coverage of graphene sheets less than three layers thick, but also the uniformity over the entire substrate. Although the better coverage rate of the graphene sheets has been demonstrated by using 150 nm thick (relative to 75 and 225 nm thick) inner Ni layer, the uniformity of the as-grown graphene could still be further improved through increasing the thickness of the inner Ni layer by several tens of nanometers to slightly increase the carbon solubility in Ni–Cu alloy. As such, extra carbon atoms can be trapped in the Ni–Cu alloy during the fast cooling process, avoiding the undesired rejection of carbon atoms to disturb the growth of graphene and to achieve the improved uniformity of the as-grown graphene sheets. In the fast-cooling step, the faster the cooling rate, the higher proportion of the dissolved carbons could still remain in the
Ni–Cu alloy because less carbons would be rejected from the Ni–Cu alloy. Consequently, a properly selected fast cooling rate of >35 °C/min may also help to improve the uniformity of the graphene sheets.

3.5. Electrical Characterization. As shown in Figure 5a, we fabricated an HMDS-derived graphene device to investigate its electrical resistance. Figure 5b shows the low sheet resistance of ~450 ohm/sq of the HMDSDerived graphene, which was mainly composed of bi- and trilayer sheets, that was synthesized from a 150 nm thick inner Ni layer catalyst. The low sheet resistance of the HMDS-derived graphene sheets provides a useful alternative candidate for transparent electroplates for future use in electronics and photonics.

4. CONCLUSIONS

We report a new method for the large-area growth of single- to few-layer graphene films. By vapor-priming HMDS onto a Si wafer followed by coating with alternating Ni/Cu/Ni catalysts, single- to few-layer HMDS-derived graphene sheets with wafer-sized dimensions could be synthesized via a CVD reaction. Micro-optical, AFM, and micro-Raman techniques were used to characterize the structural properties of the as-grown graphene. The HMDS-derived graphene sheets exhibit lower sheet resistance (~450 ohm/sq) and can be used for transparent electroplates. With a lithographic design, an HMDS-modified SiO2/Si substrate with predefined patterns can be tailored to grow graphene directly onto a Si wafer for subsequent device fabrication, thereby allowing for electronic and photonic applications. This method, therefore, has potential for future large-scale fabrication of graphene-based devices.

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Notes
The authors declare no competing financial interest.

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