Wafer-Scale Graphene Growth on Si/SiO₂ Substrates via Metal-Free **Chemical Vapor Deposition**

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 $FWHM_{2D} = 19.08$). The transfer-free graphene exhibited a Hall mobility of 1864.6 cm²·V⁻¹·S⁻¹. Moreover, an empirical formula has been developed by applying the Monte Carlo method with the measured $\frac{1}{1-k\left(\frac{1}{d^2}\right)^{0.4835}}$. This work is results to reflect the dependence of the resistivity of the graphene film on its flake size distributions as ρ =

highly compatible with present semiconductor device processing techniques and is expected to be highly desirable for Si-based graphene applications.

KEYWORDS: wafer scale, monolayer-graphene, metal-free catalyzed CVD, transfer-free, Si/SiO₂, graphene-based electronics

INTRODUCTION

Graphene, the most promising two-dimensional (2D) material, possesses exceptional chemical, mechanical, and electronic properties, opening up extensive applications across various fields.¹⁻⁴ To date, controlled synthesis of graphene remains a crucial step for realizing its diverse applications.⁵ Among the commonly used methods, including mechanical exfoliation,^{6,7} chemical vapor deposition (CVD),^{8,9} graphene oxide reduction method,^{10,11} and epitaxial growth,^{12,13} the CVD method is the one that perfectly balances effectivity, product quality, and controllability.^{14,15} Atmospheric pressure chemical vapor deposition (APCVD) is the most promising route to readily synthesize high-quality, low-cost graphene.¹⁶ APCVD has realized large-area (meter-sized),¹⁷ high-quality (singlelayer),¹⁸ and highly controllable graphene on metal sub-strates.^{19,20} Meanwhile, graphene on metallic substrates must be transferred onto dielectric substrates to be used electronically, which inevitably introduces defects and contaminations to graphene films, consequently deteriorating the performance.^{21,22} Hence, direct growth of graphene on dielectric substrates would be an ideal solution to overcome such problems.^{23,24} Much effort has been devoted to the direct growth of graphene on various dielectrics.^{25–28} For example, the growth of few-layer graphene films on a SiO₂ substrate was

that a homogeneous monolayer graphene was obtained $(I_{2D}/I_G = 4.89)$,

achieved using methane as a carbon precursor by Bi et al.²⁷ Few-to-monolayer graphene on TiO2 chips was obtained using a CH₄ precursor.²⁹ Nanosized graphene grains were directly synthesized on an Al₂O₃ substrate,³⁰ and vertically aligned graphene nanosheets were directly grown on a Si substrate using methane as a precursor.³¹ Among these substrates, Si/ SiO₂ is the most ideal substrate due to its low cost and high compatibility to silicon-based circuits.^{32,33} However, the weak catalytic ability of the substrate and the Stranski-Krastanov (SK) growth mode³⁴ can lead to poor thickness uniformity and graphene quality with small flakes and low coverage.²⁵ Till date, the main challenges are the difficulties in exact layer control, large size patch realization, and inhomogeneity of grown graphene. Therefore, how to grow high coverage, high quality, and uniform monolayer graphene is a main hurdle to be overcome.

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Figure 1. Characterization of graphene grown at different temperatures. (a) Raman spectra of graphene grown at different temperatures. (b) I_{2D}/I_G (black line) and FWHM_{2D} (red line) at 1140, 1150, 1160, and 1170 °C. (c, d) AFM images and (e, f) SEM images of the morphology of the samples grown at temperatures of 1150 °C (c, e) and 1170 °C (d, f), respectively.

Herein, we present a scheme for direct growth of a waferscale, monolayer graphene film on a Si/SiO₂ substrate using the APCVD method. Under the optimal parameters, a singlelayer graphene ($I_{2D}/I_G = 4.89$, FWHM_{2D} = 19.08) that is fully covered on a Si/SiO₂ substrate was realized with a measured Hall mobility of 1864.6 cm²·V⁻¹·S⁻¹. Moreover, an empirical formula is composed through the combination of experimental results and Monte Carlo simulation, which can be used to evaluate the flake size distribution of a graphene film through its measured electric conductivity.

RESULTS AND DISCUSSION

Growth of Graphene on Si/SiO₂ Substrates. Graphene was grown directly on Si/SiO₂ substrates using methane as a precursor under atmospheric pressure without introducing any catalyst. Among them, a N-doped (resistivity ρ : 0.002–0.004 $\Omega \cdot cm$) Si(100) with 285 nm SiO₂-thick oxide layer substrate was purchased from Suzhou Yancai Micro Nanotechnology Co., Ltd. (Suzhou, China). The substrates $(1.0 \times 1.0 \text{ cm}^2)$ were ultrasonically cleaned in acetone and isopropanol for 10 min consecutively, then rinsed with deionized water, and dried by N₂ flow. Subsequently, the substrates were placed in a corundum boat inside the quartz tube of a tubing furnace and heated to 1110-1170 °C temperature with mixed Ar and H₂ flow (120/30 sccm). After the set temperature was reached, it was maintained for 10 min both for eliminating the contaminations and relaxing the substrates' surface.³⁵ Then, methane was introduced. After the period of growth, the CH₄ gas flow was stopped, and then the sample was cooled to 400 $^{\circ}$ C at a rate of 17 $^{\circ}$ C·min⁻¹ to avoid oxidation and then cooled naturally to room temperature.³⁵ The temperature controlling curve is shown in Figure S1. The entire process includes four main steps: heating, annealing, graphene growth, and cooling.

As the most important parameters, temperature, time, and methane flow rate were systematically studied.

Effect of Growth Temperature on Graphene Quality. To investigate the influence of growth temperature on the quality of graphene, the growth time and methane flow rate were fixed at 240 min and 1.5 sccm, respectively. The Raman spectra of graphene under different temperatures were analyzed in Figure 1a. The characteristic peaks mainly include a D peak (1350 cm⁻¹), G peak (1580 cm⁻¹), and 2D peak (2700 cm⁻¹).^{36,37} The D peak is generally considered as the consequence of disorder scattering, which represents defect information of graphene samples.³⁶ The G peak is caused by the in-plane vibration of sp² carbon atoms and appears near 1580 cm^{-1} . The 2D peak is a result of the interlayer stacking mode of carbon atoms in graphene, which reflects the layer number, symmetry, and crystallinity of graphene.³⁷ To quantitatively estimate the crystallinity of graphene, the full width at half maximum of 2D (FWHM $_{2D}$) and the ratio of the 2D and G peak intensity (I_{2D}/I_G) have been analyzed. As shown in Figure 1b, the $FWHM_{2D}$ values shrink with increasing temperature from 1140 to 1160 °C and then increase again at 1170 °C (red line). The maximum I_{2D}/I_{G} = 4.12 appears at 1150 °C that implies the grown monolayer of graphene at this temperature (denoted by T-1150).³⁸ Meanwhile, the $I_{\rm 2D}/I_{\rm G}$ decrease with the increase in temperature indicates the deterioration of graphene quality.³⁹

Furthermore, when the growth temperature was set to 1140 $^{\circ}$ C, the grown sample appears as a few randomly distributed 2 nm-thick small yellowish bright spots, as shown in Figure S2a in the Supporting Information, which was further verified by the SEM image in Figure S2b. This indicates that the primary flakes experience coalescence and expansion, but no continuous film forms at this temperature.^{40,41} When the temperature increased to 1150 $^{\circ}$ C, as shown in Figure 1c,



Figure 2. Characterization of the graphene grown with different methane flow rates. (a) Raman spectra of graphene grown with different methane flow rates. (b) Measured dependence of the I_D/I_G (black line) and FWHM_{2D} (red line) on the methane flow rate. (c, d) AFM images of graphene (scan region of 10 μ m × 10 μ m) grown with methane flow rates of 1.5 and 1.6 sccm, respectively.



Figure 3. Characterization of the graphene with different growth times. (a) Raman spectra of graphene with different growth times. (b) Measured dependence of the I_D/I_G (black line) and FWHM_{2D} (red line) on different growth times. (c, d) AFM images of graphene (scan region of 10 μ m × 10 μ m) with growth times of 326 and 330 min, respectively.

almost no visible bright spots exist in the lateral force microscopy (LFM) image, which coincides with the measured excellent uniformity in the SEM image (Figure 1e). It

demonstrates the formation of uniform and continuous graphene at this temperature.^{42,43} Figure S2c exhibits the AFM result of the sample grown at 1160 $^{\circ}$ C, where the white

Figure 4. Characterization of graphene under the optimal growth parameters. (a) Five representative positions I to V were selected on grown graphene on Si/SiO₂. (b) One representative Raman spectrum measured on the sample. (c) I_{2D}/I_G mapping of the 50 μ m × 50 μ m region in which more than 99.60% of the region has $I_{2D}/I_G \ge 3$. (d) I_D/I_G mapping of the sample area in which more than 99.68% of the area has measured $I_D/I_G \le 1.5$.

spots have a size and thickness of 0.1–0.15 μ m and 3.8–4.1 nm, respectively. It is consistent with the measured dark gray spots on the surface of the sample in the corresponding SEM image (Figure S2d). A further increased temperature could grow thicker graphene films and lead to the thermal damage of the substrate. When the growth temperature increases up to 1170 °C, the surface of the grown sample becomes very bumpy. This is reflected by the large fluctuation of the measured surface profile using LFM, as shown in Figure 1d, and part of them can even be up to 5.3 nm. As shown in Figure 1f, the same results are exhibited in the SEM image as cracks and large thick flakes. The formation of cracks is mainly due to the different thermal expansion coefficients of the substrate and graphene where the dark gray circles are the domains formed by secondary nucleation.^{40,44} A small peak at 1440 cm⁻¹ is the third-order Raman peak of the TO mode of the Si-Si bond in amorphous silicon (480 cm⁻¹).^{45,46}

Effect of Methane Flow Rate on Graphene Quality. As shown in Figure 2a, when the methane flow rate is 1.4 sccm, the featured Raman signals of graphene are weak. From Figure 2b, the high I_D/I_G (ratio between the intensity of the D peak and G peak) reveals the high defect density of grown graphene. For a methane flow rate of 1.5 sccm, a distinct and narrow 2D peak appears with $I_D/I_G = 1.23$ and FWHM_{2D} = 17.77, indicating the formation of single-layer graphene. Further AFM imaging, shown in Figure 2c, displays its rather high uniformity with only minute secondary nucleation.^{47,48} With a flow rate of 1.6 sccm, the grown graphene has a blue-shifted 2D peak and $I_D/I_G = 1.25$, which indicates the formation of more than one layer of graphene.³⁶ It coincides with the AFM measurement shown in Figure 2d, where several large-area islands with a height in the range of 3–4 nm appear. Moreover, with CH₄ flow up to 1.65 sccm, the increased D peak $(I_D/I_G = 1.52)$ and broadened 2D peak (21.44 cm⁻¹) indicate the growth of multilayer graphene.³⁹ All samples are grown at a temperature of 1150 °C, and the growth time was set at 240 min in this section. The related AFM images at varying methane flow rates are displayed in Figure S5. More Raman measurements of samples grown at different methane flow rates can be found in Figure S6 of the Supporting Information.

Effect of Growth Time on Graphene Quality. Growth time is one of the key elements to determine the final number of grown graphene layers. As shown in Figure 3a, the intense D peak indicates the high defect density of grown graphene when the growth time was 280 min, which can be attributed to the highly exposed edges of graphene flakes.^{37,49} It is also confirmed by the AFM image shown in Figure S7a. When the growth time was increased to 300 min, although the intensity of G and 2D peaks did not change much, the intensity of the D peak shows an observable decrease in the measured Raman spectrum (Figure 3b). This can be attributed to the size increase of graphene flakes, consequently resulting in the lower amount of edge portion in total.^{38,50} It is also reflected in the measured AFM image of Figure S7b. After further extending the growth time to 323 min, the intensity of the 2D peak increases, the I_D/I_G decreases from 1.48 to 1.31, and the FWHM_{2D} shrinks from 21.21 cm⁻¹ (300 min) to 19.24 cm^{-1} (323 min), hinting the improvement of graphene crystallinity.³⁷ The graphene film with the highest quality was obtained with a growth time of 326 min, where the measured Raman spectra show the minimum $I_D/I_G = 1.18$, FWHM_{2D} = 19.08 cm⁻¹, and I_{2D}/I_{G} = 4.89. As demonstrated in the AFM image in Figure 3c, the grown graphene is very uniform. The Raman mapping of all randomly chosen 50 μ m \times

Figure 5. Schematic illustration of the graphene growth mechanism on Si/SiO_2 . (a) Formation of silicon dangling bonds and decomposition of the carbon precursor. Hydrogen atoms, carbon atoms, oxygen atoms, and silicon atoms are in colors green, black, blue, and purple, respectively. (b) Reaction between the CH₃ molecule and the edge of graphene. The carbon atoms in CH₃ and the graphene on the edges are in colors yellow and red to be distinguished clearly, respectively. (c) Graphene growth from small nucleation points that eventually cover the entire substrate.

Figure 6. Electrical characterization of grown graphene. (a) Image of the Hall bar and electrodes. The inset is a close-up of the actual Hall bar that has a width $W = 5 \ \mu$ m and length $l = 30 \ \mu$ m. (b) AFM image of the Hall bar, where the inset shows the height of graphene $d = 0.396 \ nm.$ (c) $I - V_{xx}$ curve of the Hall bar. (d) Hall voltage $V_{\rm H}$ measured at different magnetic fields *B* (0, 579.55, 976.45, 1431.75, and 1791.50 G) and $I_{\rm s} = 0.5, 1, 1.5,$ and 2 μ A.

50 μ m areas shows a narrow FWHM_{2D} about 20 cm⁻¹ and I_{2D}/I_{G} more than 3, as shown in Figure 4c. Again, it confirms the highly uniform monolayer nature of the grown graphene.

However, when the growth time was prolonged to 330 min and more, the intensity of the D peak starts to rise, indicating the increase in defects. The broadening of the 2D peak indicates the increase in graphene layers,³⁶ which are demonstrated as the bright large circular areas in the AFM image with the height of 6-10 nm. With a further increase in growth time, the size of multiple layer areas continues to grow (Figure 3d), and more measurements are presented in Figure S8. It is worth noting that the actual transition window from single-layer to multiple-layer growth is less than 10 min, which could be analogous to the commonly observed phase transition in physical world. Therefore, the fully single-layer covered state can be considered as one phase and the multiple layers covered as another phase, while this transition happens on the time axis.

In summary, when growth parameters are $T_{\text{growth}} = 1150 \text{ °C}$, $t_{\text{growth time}} = 326 \text{ min}$, and $P_{\text{mathene flow}} = 1.5 \text{ sccm}$, a highly uniform single-layer graphene film fully covered on the Si/SiO₂ surface was realized without any metal catalyst.

Mechanism of Graphene Synthesis on Si/SiO_2 Substrates. As shown in Figure 5a, under the hydrogen atmosphere at certain temperature, the silicon oxide starts to decompose and form free dangling silicon bonds.^{25,51} The introduced methane molecules tend to adsorb to the clean silicon surface to break into carbon radicals.⁵² Since the strength of silicon dangling bonds is relatively weak compared to average stable chemical bonds, carbon radicals cannot anchor but only diffuse over short distances.⁵² Due to the 5.90 eV reaction barrier between methane and the graphene edge, methane is not an ideal direct feedstock for graphene growth.⁵ Meanwhile, CH₃ exhibits high reactivity due to the existence of an unsaturated bond and opt to adsorb on the surface through dangling bonds.^{54,55} In fact, CH₃ acts as the dominant carbon species, supplying carbon for graphene growth and removing excess H atoms from the edge of graphene (Figure 5b).⁵² The CH₃ molecule reacts with carbon atoms to form new carbon rings that facilitate the formation of graphene. The growth process starts from small nucleating points that expand and coalesce, eventually forming continuous films with larger flake sizes (Figure 5c).⁵⁶ The XPS analyses of graphene and Si/SiO₂ substrates are presented in Figures S9-S12 of the Supporting Information.

Electric Characterization of the Grown Graphene Film. The grown graphene was directly patterned for Hall mobility testing. A permanent tablet magnet provides an external magnetic field. To ensure the uniformity of the penetration field through the sample, the size of the magnet must be large enough and the sample must be centered on the top of the magnet. The field was adjusted through changing the distance between the sample and the magnet by shimming and measured by a well-calibrated Gauss meter (Coliy Technology G201). The Hall coefficient can be extracted from $R_{\rm H} = \frac{V_{\rm H} \cdot d}{I_{\rm c} B}$, where $V_{\rm H}$ is the Hall voltage (V), d is the thickness (m), I_s is the current (A), and B is the magnetic induction intensity (T). The sample thickness was measured using AFM. Mobility was calculated by the definition of $\mu = \frac{R_{\rm H}}{\rho_{\rm xx}}$, where $\rho_{\rm xx}$ is the resistivity. It was obtained from the formula $\rho_{xx} = \frac{R_{xx}S}{l}$, where R_{xx} is the resistance, S is the crosssectional area, and l is the channel length (Figure 6a). Here, the channel width $W = 5 \ \mu m$, length $l = 30 \ \mu m$, and d = 0.396nm (Figure 6b). The resistance is calculated as $R_{xx} = \frac{V_{xx}}{I} = 6932.66 \ \Omega$. The resistivity $\rho_{xx} = 4.58 \times 10^{-7} \ \Omega$ · m (Figure 6c). With $I_s = 0.5$, 1, 1.5, and 2 μ A, the Hall voltages were measured with the magnetic fields, as shown in Figure 6d; where measured with the magnetic fields, as shown in Figure od, therefore, $R_{H1} = 9.77 \times 10^{-8} \text{ m}^3/\text{C}$, $R_{H2} = 9.62 \times 10^{-8} \text{ m}^3/\text{C}$, $R_{H3} = 8.84 \times 10^{-8} \text{ m}^3/\text{C}$, and $R_{H4} = 8.54 \times 10^{-8} \text{ m}^3/\text{C}$, respectively, and the calculated Hall mobilities are $\mu_1 = 2133.2$ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$, $\mu_2 = 2100.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$, $\mu_3 = 1930.1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ S⁻¹, and $\mu_4 = 1864.6$ cm²·V⁻¹·S⁻¹, respectively.

Assuming that all graphene flakes are single crystals, when current run through a graphene flake forming a continuous film, the flake distribution determines the number of boundaries, and therefore, the scattering rate of charge carriers will be experienced.^{57–59} Smaller flake-assembled films will have more boundaries than the one composed of larger flakes. Hence, more scattering occurs when charge carriers run through the same distance, consequently exhibiting a higher resistivity. To get a better understanding of the relation between the size distribution of graphene flakes and the macroscopic resistance of the continuous film what it made of, a simple classic model was proposed by assuming that there is a constant momentum loss each time when a charge carrier crosses the boundary. Numerical simulations have been

conducted through Monte Carlo (MC) and Voronoi methods.^{60,61} Table 1 summarizes the average flake areas, scattering times, and variances from the average area for the four different size distributions.

Table 1. Distribution	of Scattering	Rate and	Flake Area
Variance $\sigma (A_{max})^a$	_		

		dependent variable	
d_{\min}	$A_{\rm mean}~({\rm nm}^2)$	scattering times	σ (A)
$0.2\overline{d}$	405.5769	132.6801	214.1587
$0.4\overline{d}$	404.2293	131.1569	171.266
$0.6\overline{d}$	404.0073	131.4087	109.6981
$0.8\overline{d}$	404.8574	128.2088	62.0257

 ${}^{a}d_{\min}$ is the minimum distance between crystal nuclei points, \overline{d} is the average flake size. 10,000 flakes are sampled. The flake size *d* is defined as the length on the longest dimension of the flake.

In Figure 7a–d, the graphene flakes with different $d_{\min} = 0.2$, 0.4, 0.6, and 0.8 \vec{d} are presented. Through fitting the measured resistivity of the graphene film with the flake size distribution (Figure 7e), we obtained the relation between the film resistivity and the average graphene flake size as $\rho = \frac{\rho_0}{1 - k \left(\frac{1}{\lambda^2}\right)^{0.4835}}$

, where ρ_0 is the resistivity of single-layer pristine graphene, k is a constant equal to 5.82, and d is the average size of flake. The fitted curve can be used to qualitatively predict the average size of graphene flakes through its resistivity measurement (Figure 7f). The numbers of scattering almost show no dependence on the flake uniformity, and more detailed discussions and simulation results can be found in the Supporting Information.

CONCLUSIONS

In summary, we have successfully realized the direct growth of single-layer graphene fully covering a centimeter-scale Si/SiO₂ substrate without introducing any external catalyst. Its high quality was confirmed by the Raman results with $I_{2D}/I_G = 4.89$ and FWHM_{2D} = 19.08 and the measured 1864.6 cm²·V⁻¹·S⁻¹ Hall mobility as well as the extremely high uniformity reflected both in the AFM and SEM imaging. In addition, a model was built that can simply extract flake size information through its electric resistivity measurement. These results provide vital information for direct growing high-quality graphene on dielectric substrates without metallic catalysts, which could be significant to the graphene-based electronic industry in the future.

EXPERIMENTAL SECTION

Characterization of Graphene. The morphology of samples was characterized using an Optical Microscope (WY-2000M), scanning electron microscope (Hitachi SU3500) with 15 kV beam energy, and atomic force microscope (Park NX10) in contact mode. A Raman confocal spectrometer (532 nm laser excitation, $100\times$ objective lens, laser power 5 mW) was used to measure the quality and featured peaks of graphene. XPS measurements were carried out using a Perkin-Elmer, PHI 5100 with Al K α line.

Preparation of Hall Bar and Its Performance Test. The fabrication of hall bar is shown in Figure S16. Patterning of graphene was carried out directly on the grown graphene on the Si/SiO_2 substrate. The effect of high temperature on the SiO_2 dielectric layer is also considered in Figure S17. Reactive ion etching (RIE) with oxygen plasma was used to remove excess graphene and residual photoresist. The etching was performed in a RIE system (Model 150, Tailong Electronics, Beijing, China) with an RF power of 35 W and

Figure 7. Flake size distribution and its corresponding resistivity. (a-d) Distribution of flake sizes. (e) Relation between the flake number and scattering rate, where the black dots are the simulated scattering rate using the MC method and the red line is the fitting result. (f) Relation between the average flake size and resistivity. The red line represents the fitting results, and black dots represent the experimental results.

an O_2 flow of 50 sccm for 30 s. Subsequently, the samples were immersed in acetone, isopropanol, and deionized water sequentially to remove the photoresist. The next step is to prepare source and drain electrodes by depositing 20 nm/10 nm-thick Cr/Au with a rate of 0.3 A·s⁻¹/0.1 A·s⁻¹ using an electron beam evaporator and consecutively followed by a lift-off procedure in acetone. Hall mobility and sheet resistance were measured using a four-probe method through a cryogenic probe station (Lakeshore TTPX) with two source meters (Keithley 2450) at room temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.3c01956.

Temperature controlling curve, AFM and SEM images of morphology; Raman spectra of the graphene film; XPS analyses of graphene and Si/SiO₂ substrates; flake size distribution and scattering rate; flake uniformity distribution; position ranges and scattering rate frequency distribution; schematic illustration of the Hall bar fabrication process; I-V curve of the Si/SiO₂ substrate before and after annealing (PDF)

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Author Contributions

L.M. and Y.M. supervised the project. L.M. conceived and designed the experiments. M.L. performed the experiments of graphene growth and the characterization of materials. P.Z. developed the theoretical model and data simulation. Z.C., R.Z., C.T., and S.W. analyzed the data and discussed the results. M.L. wrote the manuscript. L.M. and Y.M. revised and edited the manuscript. All authors contributed to the manuscript preparation.

Notes

The authors declare no competing financial interest.

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