Practical Route for the Low-Temperature Growth of Large-Area Bilayer Graphene on Polycrystalline Nickel by Cold-Wall Chemical Vapor Deposition

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ABSTRACT: We report a practical chemical vapor deposition (CVD) route to produce bilayer graphene on a polycrystalline Ni film from liquid benzene (C6H6) source at a temperature as low as 400 °C in a vertical cold-wall reaction chamber. The low activation energy of C6H6 and the low solubility of carbon in Ni at such a low temperature play a key role in enabling the growth of large-area bilayer graphene in a controlled manner by a Ni surface-mediated reaction. All experiments performed using this method are reproducible with growth capabilities up to an 8 in. wafer-scale substrate. Raman spectra analysis, high-resolution transmission electron microscopy, and selective area electron diffraction studies confirm the growth of Bernal-stacked bilayer graphene with good uniformity over large areas. Electrical characterization studies indicate that the bilayer graphene behaves much like a semiconductor with predominant p-type doping. These findings provide important insights into the wafer-scale fabrication of low-temperature CVD bilayer graphene for next-generation nanoelectronics.

1. INTRODUCTION

Graphene, a two-dimensional material of sp2-bonded carbon atoms arranged in the form of a hexagonal lattice structure, has been a topic of great interest, both in scientific and technological communities, ever since its discovery in 2004.1 Owning to its outstanding physical and chemical properties, it has been extensively selected as a material for various novel applications in energizing the fields of nanoscience and nanotechnology. Yet, the absence of a band gap for single-layer graphene greatly restricts its use in most electronic applications such as digital logic circuits and photonic devices.2,3 With most electronic applications relying on the presence of a band gap, the recent signature of the band gap opening induced in bilayer graphene under an external transverse electric field across the two layers,4 making it beneficial for next-generation optoelectronic and nanoelectronic devices even though the opened band gap is not greater than 0.25 eV. Interestingly, this expected band gap opening from the mid infrared to the far infrared enables bilayer graphene to be tuned from a metal to a semiconductor through the gate bias or charge-transfer doping5−7 which cannot be achieved in any state-of-the-art semiconductors. Moreover, bilayer graphene with a proper control stacking orientation between the two layers is anticipated to have better electrical conductivity and induced insulating–superconducting states that are completely absent in single-layer graphene, which have been proven to be most attractive on graphene electronics.8,9 Over the last decade, scientists have been competing to develop a promising method for synthesizing scalable high-quality bilayer graphene using various synthesis techniques. In most of the experiments, a viable method of chemical vapor deposition (CVD) has shown great promise for producing relatively high-quality bilayer graphene on Cu,10−12 Ni,13−15 or Cu–Ni alloy16,17 due to its industrial scalability, economic efficiency, and acceptance by the semiconductor industry. Based on the general strategies of growing graphene by CVD at high temperatures, the formation of bilayer graphene via the Ni surface-mediated reaction method is much easier to be controlled with Cu as it has the lowest carbon solubility and

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carbon affinity compared to other metals such as Ni or Co.\textsuperscript{18} For instance, lowering the graphene growth rate by adopting an extremely low hydrocarbon concentration simply promotes the second graphene layer growing underneath the first graphene layer.\textsuperscript{13} However, the coalescence of the graphene domains driven by the self-limiting process on Cu may often restrict the growth of the second graphene layer beneath and eventually leads to low coverage of bilayer graphene.\textsuperscript{20} On the other hand, in the case of Ni, a more uniform bilayer graphene growth can be achieved via a precipitation method, but the mechanism is more complex with the variables of carbon dissolution–precipitation\textsuperscript{21,22} and cooling process.\textsuperscript{15} Furthermore, the high solubility of carbon and the metastability of carbide formation in Ni stimulate the nonequilibrium carbon precipitation to form multilayers during the cooling process, and it is very challenging to achieve good graphene uniformity and layer control on the surface at high pressure and temperature, especially at the grain boundaries of polycrystalline Ni.\textsuperscript{23}

For the precise control of the macroscopic scale bilayer graphene, a strategy to establish surface-mediated growth of bilayer graphene using Ni is possible with two key growth aspects: selection of aromatic hydrocarbons and lowering the processing temperature. First, the use of aromatic hydrocarbons with a specific chemical structure such as benzene,\textsuperscript{24} hexachlorobenzene,\textsuperscript{25} or toluene\textsuperscript{26} is mostly recommended due to its low activation energy required for dehydrogenation and nucleation on the catalyst surface at low temperatures as low as 100 °C. Importantly, the quality of graphene produced by this approach appears to be comparable to that obtained by using methane.\textsuperscript{10} Second, recent reports indicate that low processing temperatures determine the low solubility of carbon in the Ni substrate.\textsuperscript{27,28} As for a thin Ni film, a finite dissolution of carbon atoms on the surface occurs by kinetically controlled local surface saturation of carbon at low temperatures as suggested previously,\textsuperscript{29} thus making it desirable to produce uniform graphene with controllable layers. However, lower temperatures may deteriorate the degree of graphitization and eventually lead to poor electrical conductivities. In view of this, it is therefore important to investigate and understand the basic growth mechanism of bilayer graphene at low temperatures, which will be of key importance for the temperature-compatible graphene-based devices in next-generation electronics.

Here, we systematically study a scalable growth of bilayer graphene on a polycrystalline Ni film using benzene as the carbon precursor at low-temperature regimes by a CVD method in a vertical cold-wall reaction chamber, which are of rapid growth, less power consumption, economical, and scalable for industrial applications. Using the optimized growth conditions in a vertical cold-wall reaction chamber, we also demonstrate the growth capability of large-area bilayer graphene on an 8 in. wafer-scale substrate at a temperature as low as 400 °C, which is rarely achieved with conventional tube furnace systems, that is, horizontal hot-wall reaction chambers.\textsuperscript{30} Raman spectra analysis, high-resolution transmission electron microscopy, and selective area electron diffraction confirm that bilayer graphene was successfully grown on a polycrystalline Ni film. Both the results of electrical transport, including Hall effect measurements and back-gated field-effect transistor studies, demonstrate that our bilayer graphene exhibits excellent sheet resistance and mobility, suggesting its suitability for potential integration in the future nanoelectronic devices.
2. RESULTS AND DISCUSSION

2.1. Structural Characterization of Bilayer Graphene. Raman spectra measurements of graphene growth at 400 °C were first examined on three different points (a, b, and c) to verify the number of the constituent graphene layers on the SiO₂/Si(100) substrate, as shown in Figure 1a. Prior to the Raman spectra measurements, the system was calibrated using a commercial CVD pristine single-layer graphene (Graphenea, Inc.) with a typical 2D peak position at 2700 cm⁻¹. One of the most important parameters in determining the number of graphene layers is the ratio of 2D band intensity to G band intensity \((I_{2D}/I_G)\), where the intensity ratio, \(I_{2D}/I_G\) for single-layer graphene is more than 2, bilayer graphene is about 1, and multilayer graphene is less than 1.31 In this work, the mean value of the \(I_{2D}/I_G\) ratio is estimated to be 0.52 at point a (dark region) and 1.06 at point b (light region), indicating the multilayer and bilayer graphene. Meanwhile, the mean value of \(I_{2D}/I_G\) is about 2.93 at point c (light region) and almost comparable to that of pristine single-layer graphene. In addition, it should be noted that the full width at half-maximum (fwhm) of a 2D peak is often used to determine the number of graphene layers based on previous empirical works.32 34 A single layer (20–35 cm⁻¹), bilayer (35–50 cm⁻¹), and multilayer (more than 60 cm⁻¹) Raman maps intensity of \(I_{2D}/I_G\) and the fwhm of the 2D peak, as shown in Figure 1b,c, the bilayer graphene film was determined as a dominant area with almost 85.5 ± 2.5% coverage, while the remaining areas of 9.6 ± 3.6 and 4.9 ± 1.6% were covered by the single-layer graphene and multilayer graphene patches, respectively. Another important parameter in evaluating the degree of the defects could be the ratio of D band intensity to G band intensity \((I_D/I_G)\). The mean values of the \(I_D/I_G\) ratio for points a, b, and c are determined to be 0.11, 0.30, and 3.42, respectively. The \(I_D/I_G\) ratio shows a strong dependence on the number of graphene layers with increasing defects in the order of point c > b > a, which is also consistent with the Raman map intensity of \(I_D/I_G\), as shown in Figure 1d. In particular, the increase in the intensity of D band to G band intensity \((I_D/I_G)\) at 1353 cm⁻¹ suggests that much higher defects are predominant and easily induced at the thinner layers.65 This can relatively contribute to the additional D' and their combination mode \((D + D')\) peaks at 1621 and 2953 cm⁻¹, which are activated by a single-phonon inter-valley and intra-valley scattering process.31 The higher \(I_D/I_G\) ratio can be possibly attributed to the presence of an interfacial carbon layer at the C–Ni interface or incomplete graphene layer with sp² carbon in the form of a nanocrystalline domain during the growth process. Next, it is noted that the shape and frequency of the 2D band are dependent on the number of graphene layers. The distinct band shape differences of the 2D band at points a, b, and c are shown in Figure 1f. At point c, the single-layer graphene film shows a narrow and symmetric Lorentzian 2D and the peak position at 2700 cm⁻¹ is comparable to that of pristine single-layer graphene. Meanwhile, at point b, the asymmetric 2D band of bilayer graphene was shifted to a higher frequency in relation to that of single-layer graphene with average blue shifts of 9 cm⁻¹ and consists of four components: 2D₁, 2D₂, 2D₃, and 2D₄ at 2632.9, 2699.8, 2735.4, and 2769.6 cm⁻¹, respectively. Similarly, as the number of graphene layers increases in the multilayer stack at point a, the asymmetric 2D band of multilayer graphene was also shifted to a higher frequency with average blue shifts of 26 cm⁻¹. Here, two components in the deconvoluted 2D band corresponding to 2D₁ and 2D₂ were presented at 2689.6 and 2739.5 cm⁻¹, respectively.

Raman spectra measurements for graphene growth at much lower temperatures were also investigated to confirm possible graphene formation on the same Ni film substrate. From the Raman spectra results by the point scan method at a thin region, as shown in Figure 1g, the D, G, and 2D bands show a strong dependence on the growth temperature with different peak intensities. It was noticed that the intensity of G and 2D bands significantly decreased as the temperature decreased to 100 °C, indicating predominant unwanted amorphous carbon layers or incomplete graphene growth.24 Meanwhile, at 25 °C, graphene was not fully synthesized on the Ni surface. Our findings suggest that it is impossible to synthesize graphene on the Ni surface at temperatures below 200 °C due to low dehydrogenation rate of C₆H₆ molecules, which is in good agreement with previous experimental observations and theoretical predictions based on first-principles calculations.32 Furthermore, lowering the growth temperature may also degrade the graphene quality and result in a higher degree of defects, where the mean value of the \(I_D/I_G\) ratio drastically increased up to 2.63 as the growth temperature decreased to 100 °C. It is noted that the \(I_D/I_G\) ratio is usually related to the disorder degree in the in-plane graphene, which can be determined by quantifying the defect density,33 \(n_d = [(1.8 ± 0.5) × 10^{22}] \cdot \lambda^2 \cdot (I_D/I_G)\), where \(\lambda\) is the laser excitation wavelength. The \(n_d\) for the graphene growth as a function of growth temperature is shown in Figure 1h, where the defect density increases as the growth temperature decreases. This finding implies that low temperatures (≤300 °C) might decelerate catalytic dehydrogenation reaction of C₆H₆ molecules and increase the probability of defects, thus eventually leading to the poor crystallinity of graphene layers. Similarly, this finding also correlates well with the observed high-resolution transmission electron microscopy (HR-TEM) images (see Figure S1 in the Supporting Information), showing that our graphene layers are polycrystalline in nature and composed of many single-crystal domains separated by atomically grain boundaries or defects as the growth temperature decreases. On the other hand, for the growth process at high-temperature regimes, the mean value of the \(I_D/I_G\) ratio gradually decreased from 0.29 to 0.17 as the growth temperature further increased from 500 to 700 °C, suggesting a slight improvement in graphene quality (see Figure S2 in the Supporting Information). Despite this, the growth processes above 500 °C mostly result in few-layer or multilayer graphene. Therefore, as a good tradeoff between the graphene quality, growth temperature, and thickness control, we only consider the growth process at 400 °C for further characterization of bilayer graphene.

On the basis of the CVD method, a simple growth model can be proposed for the formation of the graphene layers via Ni surface-mediated reaction. It is noted that the growth process consists of three stages: catalytic dehydrogenation, nucleation and expansion, and formation of continuous layers. Upon introducing the C₆H₆ precursor with supported Ar carrier gas at low temperatures, the C₆H₆ molecules are directly adsorbed on the catalytic Ni surface and decomposed to form highly activated six-ring carbon species by catalytic dehydrogenation with Ni. It is noted that the carbon solubility in the Ni film at low temperatures (≤400 °C) is considered negligible as the carbon dissolution into the bulk is limited.26
The graphene growth here focuses on low temperatures and relatively low pressure, in which the CVD process is surface reaction controlled. The possible catalytic surface reaction to produce graphene can be expressed by the following equilibrium: $\text{C}_6\text{H}_6 + \text{Ar} + (\text{Ni})_{\text{surface}} \rightleftharpoons (6\text{NiC})_{\text{surface}} + 3\text{H}_2 + \text{Ar}$, where $(\text{NiC})_{\text{surface}} \rightleftharpoons (\text{Ni})_{\text{surface}} + \text{graphene}$. Using a vertical gas flow over the Ni surface, where the substrate is directly in contact with the hot stage, surface adsorption of the activated six-ring carbon species possibly takes place across the surface until reaching the limit of Ni solubility, and a local carbon supersaturation starts to develop graphene nuclei at the initial nucleation stage. Here, accumulation of the activated six-ring carbon into oligomeric $(\text{C}_x\text{H}_y)_n$ species may also occur before going to be the final hydrogen-free product on the Ni surface and result in the formation of bilayer or multilayer nuclei, especially at the grain boundaries. Further migration of the reactive six-ring carbon species into the edges of graphene nuclei facilitates the expansion of the first layer and the second layer underneath the first layer to assemble bilayer graphene spontaneously prior to the completion of the first layer. We assume that the growth of additional graphene layers is coexistent and dependent on the first layer with the inherent polycrystalline of graphene whereby the domain boundaries and other defects offer pathways for carbon to reach the Ni surface. Here, the adlayers in graphene grow underneath the already grown graphene coverage.

Figure 2 shows the features of the graphene layers that were obtained on an optimum 150 nm-thick Ni film on the SiO$_2$/Si(100) substrate at a growth temperature of 400 °C. Figure 2a shows an optical micrograph of the as-grown bilayer graphene on the Ni film, where the resultant graphene growth exhibits continuous layers in the morphology of mostly bilayer (lighter region) and numerous micro-sized islands (darker region) on the underneath bilayer graphene, which can also be observed as multilayer graphene patch. Based on the visibility of color contrast, the presence of the continuous bilayer and the multilayer graphene patch can be seen through the FESEM image and optical micrograph in Figure 2b,c. In this work, it is almost impossible to eliminate the formation of the multilayer patch at the grain boundaries of Ni crystallites with small grain size ranging from 100 to 500 nm. However, the density of the multilayer patch can be well controlled by tuning the Ni film thickness. From the optical micrographs (see Figure S3 in the Supporting Information), it seems that the density of the multilayer patch increases by increasing the film thickness up to 300 nm. The multilayer patch is highly preferred on the 300 nm-thick Ni film, implying that the catalytic dehydrogenation reaction occurs sufficiently on the Ni surface, thus leading to the formation of multilayers. In contrast, the multilayer patch is least observed on the 150 nm-thick Ni film due to higher carbon saturation throughout the thinner Ni film, where the number of the reactive six-ring carbon species available on...
the surface is limited to be incorporated into the edges of the graphene nuclei. X-ray photoemission spectroscopy (XPS) studies were also performed to evaluate the purity of the as-grown bilayer graphene on the Ni film and the as-transferred bilayer graphene on the SiO2/Si(100) substrate (see Figure S4 in the Supporting Information). The sample shows the presence of a typical C 1s and O 1s peak located at ∼284 and ∼532 eV, respectively. Here, the core level C 1s spectra are fitted with four components, which consist of the main peak at ∼284.4 eV corresponding to the C≡Cs p2 and the other lower peaks with higher binding energies at ∼285.8, 286.8, and 289.2 eV corresponding to the typical C−OH, C≡O, and −COOH bonds presented at the basal plane and edges, respectively. These lower peaks might appear due to the presence of structural defects or surface contaminants accumulated during atmospheric exposure. Importantly, the spectrum shows no prominent peaks corresponding to Ni 2p located at ∼850 to ∼880 eV, suggesting that the bilayer graphene transferred on the SiO2/Si(100) substrate is free of the residual Ni or NiO nanodots on the graphene surface.

In order to investigate a cross-sectional view of a layer-by-layer structure, a 90 nm thick lamella was first-extracted locally from a region of the bulk sample and subsequently further thinned with a focused ion beam prior to high-resolution imaging in the TEM. Figure 2d,e shows the TEM cross-sectional images of the bilayer graphene sample with the 150 nm thick Ni film. The bilayer graphene was confirmed locally through direct observation of the edges of the graphene layer from high-resolution imaging (indicated by a yellow box). Two layers of graphene stacking with an interlayer lattice spacing of 3.45 Å were obtained, as shown in the inset of Figure 2e. Meanwhile, multi-layer graphene formation was also identified in other HR-TEM images (see Figure S5 in the Supporting Information) as further evidence to support the Raman analysis. It should be noted that the homogeneity of the graphene growth is strongly dependent on Ni crystallites and some parts of polycrystalline Ni have (111) Ni atomic arrangement, which is nearly atomically coherent with the basal plane of the graphitic layers for the lateral growth direction.23,34 For the growth temperature of 400 °C, our HR-TEM images indicate that a combination of the Ni crystallite orientations [e.g. Ni(111) and Ni(200)] separated by the grain boundaries as shown in Figure 2f,g may result in a large-area bilayer graphene growth with minor multilayer graphene patches, which exhibits a similar topography to the recent report of bilayer graphene at high temperature.14 Here, the lattice constant for Ni(111) and Ni(200) was determined to be 2.07 and 1.77 Å, respectively. To correlate these results, the XRD spectra of the samples after the annealing and growth process were collected and compared to a bare SiO2/Si, as shown in Figure 2h. The bilayer graphene sample shows a small distinct peak at ∼26.5°, which is attributed to the (002) reflection of the graphitic carbon. Meanwhile, no carbon peak (002) is presented for the annealed sample, which means that graphene growth is totally absent. The samples also display few diffraction peaks at 2θ of 44.2, 51.6, and 76.4° corresponding to the (111), (200), and (220) planes of the face-centered cubic Ni, respectively. More importantly, no significant peaks

Figure 3. Characterization of the atomic structure of graphene layers. (a) TEM image of bilayer graphene on a lacey carbon-coated Cu grid. (b) HR-TEM image of bilayer graphene in a pink box in (a). The inset shows the FFT pattern. The black dots circled with red dashed lines are sp3 point defects corresponding to contaminants. (c) Filtered HR-TEM image in the yellow box in (b). (d) Profile plots of an atomic structure along both zigzag and armchair direction in (c). (e) TEM image shows a typical multilayer graphene patch (region b) underneath large-area bilayer graphene (region a). The inset shows the HR-TEM image of multilayer graphene in region b. (f,g) SAED pattern of a bilayer and multilayer graphene. (h,i) Their corresponding profile plots of diffraction spot intensities along the red arrow in (fg) indicate AB-stacking configuration.

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were observed at ~46.3 and 49.1° corresponding to the (110) and (006) planes of the rhombohedral Ni$_3$C, implying that no carbon dissolution–precipitation process takes places in the Ni film during the isothermal growth. In this work, the large-area bilayer graphene grown on this polycrystalline Ni grains can be obtained, even with a high density of Ni grain boundaries. Nevertheless, some possible defects induced by a high density of the grain boundaries are expected to develop along the Ni surface following the low-temperature process. In some cases, it was demonstrated that high-quality graphene growth is preferentially on a Ni(111) single crystal, but a precise parameter controlling over the large-area graphene film has yet to be achieved at such low temperatures due to limited surface absorption or segregation of carbon species. The evidence of the bilayer graphene here can also be found by comparing its optical transmittance spectra with that of the single-layer graphene, as shown in Figure 2i. In such a wavelength regime, both the single-layer graphene and bilayer graphene are highly optical transparent with a specific transmittance of 97.7 and 95.4% at 550 nm in agreement with both the theoretical and experimental values. Further observations through naked eyes have also shown their distinct optical transparency, suggesting the increase in opacity of the bilayer graphene over the single-layer graphene (see the inset of Figure 2i). Next, the surface morphologies of bilayer graphene were further investigated by performing AFM measurement. Figure 2j illustrates a typical AFM image of the bilayer graphene films, where the step height from the height profile across the blue line (from graphene layers to SiO$_2$) roughly indicates the number of graphene layers. The AFM results show that the average thickness is about 1.07 ± 0.12 nm with an average RMS roughness of 0.92 nm, suggesting a good formation of bilayer graphene.

The atomic structure of the graphene layers was characterized by HR-TEM and selective area electron diffraction (SAED). Figure 3a shows the low-resolution bright-field TEM image of the bilayer graphene transferred on a lacy carbon-coated Cu grid. Large-area bilayer graphene (a few thousand square nanometers) was observed, which is highly electron-transparent even in comparison to the lacey carbon support. The most transparent areas are likely to be bilayer graphene, where the color contrasts of the layers indicate the formation of folding structures with each other during the wet chemical transfer method. Interestingly, the as-grown bilayer graphene in the present work shows fewer wrinkles compared to typical graphene growth from 800 to 1000 °C. The HR-TEM image of bilayer graphene, as shown in Figure 3b illustrates a single-crystalline nature of the graphitic domains in the form of a hexagonal lattice structure. Similarly, fast Fourier transform (FFT) patterns confirmed a single set of six-fold spots corresponding to the graphene {0−110} plane without any possible lattice mismatch or misorientation between the graphene stacking layer. Meanwhile, several black dots (indicated by a red dashed circle) were also randomly presented corresponding to contaminants, where carbonaceous adsorbates and also heavier adatoms are trapped. The individual carbon atom in the hexagonal packing arrangement can also be resolved from the Fourier filtered HR-TEM image of the bilayer graphene, as shown in Figure 3c, yet the defects are almost impossible to be probed here. It is noted that the image was carefully post-processed from the raw HR-TEM image (indicated by the yellow box) in Figure 3b by using the Fourier mask filtering method, similar to previous work. Here, the line profile contrast intensities along the zigzag and armchair direction reveal a lattice parameter of 2.46 Å and a nearest-neighbor distance of 1.42 Å, respectively (see Figure 3d). In addition, SAED characterization was also carried out on both regions A and B in order to evaluate the stacking configuration of the graphene layers (see Figure 3e). The resultant SAED patterns, as shown in Figure 3f,g, exhibit a single set of hexagonal diffraction pattern characteristics and the first-order intensity of {0−110} is likely

Figure 4. Electrical characterization of bilayer graphene. (a) Temperature dependence of resistance of bilayer graphene on the SiO$_2$/Si(100) substrate. (b) Arhenius plot of bilayer graphene on the SiO$_2$/Si(100) substrate. (c) Carrier mobility as a function of temperature. (d) Schematic representation of the back-gated bilayer graphene-FET device structure. The optical image of the device showing a 25 μm channel length and a 100 μm channel width. (e) Source−drain current ($I_{sd}$)−source drain voltage ($V_{sd}$) characteristics. (f) Source drain current ($I_{sd}$) with varying backside gate voltage ($V_g$) for the device.
seen to be much lower compared to the second-order intensity of \{1−210\}. On the basis of the analysis labeled by Bravais–Miller indices, the intensity ratios of \( I_{1−110}/I_{1−210} \) and \( I_{1−1010}/I_{1−2110} \) for the bilayer and multilayer graphene are determined to be \( \sim0.39 \) and \( \sim0.29 \), respectively (see Figure 3h,i), which are consistent with the Bernal-stacked bilayer and multilayer graphene.42

2.2. Electrical Characterization of Bilayer Graphene.

To determine possible transport of the bilayer graphene, an analysis of temperature \((T)\) dependence of the electrical resistance \((R)\) was carefully performed at a temperature range of 100 to 350 K. The relation between temperature and resistance indicates that the bilayer graphene in this work behaves much like a semiconductor \((dR/dT < 0)\) and consistent with our previous works,43,44 where resistance decreases monotonically by increasing the temperature up to 350 K, as shown in Figure 4a. Here, the negative value of the slope \((dR/dT)\) is attributed to the electrons activated from the valence band to the conduction band, which are driven by a thermal activation mechanism. Furthermore, it is known that with an increase in temperature, p-type doping in graphene increases through the SiO\(_2\) substrate, which may be the cause of a decrease in resistance as well. Here, a decrease in resistance could be originated from an increase in hole concentration due to unintentionally doping in bilayer graphene induced by the SiO\(_2\) substrate. Figure 4b shows the \( \ln(R) \) versus \( T^{-1} \) plot of bilayer graphene with a linear fitted line that represents the Arrhenius equation: \( R = A_0 \exp(-E_a/k_B T) \), where \( A_0 \) is the pre-exponential factor, \( k_B \) is the Boltzmann constant, and \( E_a \) is the activation energy representing the energy band gap for the thermal activation process.

The linear plot at a high-temperature regime, ranging from 250 to 350 K, indicates that thermally activated conduction with an estimated \( E_a \) of 27.2 meV occurs in the bilayer graphene. In this work, the activation energy of the bilayer graphene is much lower compared with that of bilayer graphene grown via a PECVD method because of the inclusion of low density of defects in its atomic structure.45 This observation suggests that a band-like transport dominates the carrier transport in the bilayer graphene, which is further confirmed by a trend of decrease in carrier mobility with increasing temperature (see Figure 4c). Further electrical characterization was performed on a 1.0 cm \( \times \) 1.0 cm sample size using a typical van der Pauw method under ambient air at 300 K by a Hall effect measurement system. The Hall mobility \((\mu_{\text{Hall}})\) of bilayer graphene transferred on the SiO\(_2\)/Si(100) substrate reaches up to 710 cm\(^2\) V\(^{-1}\) s\(^{-1}\) with a low average Hall effect coefficient \((R_{\text{Hall}})\) of 0.165 cm\(^2\) V\(^{-1}\) C\(^{-1}\), sheet concentration \((n)\) of 3.78 \( \times \) 10\(^{12}\) cm\(^{-2}\), and sheet resistance \((R_s)\) of 370 \( \Omega \) sq\(^{-1}\). The positive value of the average \( R_{\text{Hall}} \) indicates that holes are the predominant charge carriers in the bilayer graphene. For comparison with the previous CVD method, our bilayer graphene exhibits a much lower average \( R_s \) as compared to that of single–bilayer graphene grown on Cu at 1050 °C (\( \sim1300 \Omega \) sq\(^{-1}\)),46 bilayer graphene grown on Cu at 1060 °C (\( \sim560 \Omega \) sq\(^{-1}\)),47 and bilayer graphene grown on Ni at 1000 °C (1990 \( \Omega \) sq\(^{-1}\)) but slightly higher than the value reported for bilayer graphene grown on the Cu–Ni alloy at 1000 °C (\( \sim287 \Omega \) sq\(^{-1}\)).48

For further electrical measurements, the back-gated field-effect transistor (FET) by using the bilayer graphene was fabricated and annealed at 300 °C for 1 h in a vacuum condition to eliminate the possible contamination and restore clean surfaces of graphene. The bilayer graphene-FET structure is as follows from the bottom of the device: back gating of a p-type Si, 100 nm layer of SiO\(_2\) bilayer graphene and 120/60 nm layers of Pt/Ti electrodes (see Figure 4d). The bilayer graphene, bridging the source and drain electrodes,
behaved as the conducting channel. Figure 4e shows the typical source–drain current ($I_{sd}$) versus the source–drain voltage ($V_{sd}$) for the device before and after annealing. The as-annaeled device displays a linear $I_{sd}$ versus $V_{sd}$ curve over a wide range of gate voltage ($V_g$) with low contact resistance, indicating a good Ohmic contact between the Pt/Ti electrodes and the bilayer graphene. Besides, the device exhibits strong gate-tunable $I_{sd}$ characteristics under different polarities of $V_g$. The slope of the $I_{sd}$ versus $V_{sd}$ curve decreases as the $V_g$ increases from $-10$ to $10$ V. Figure 4f shows asymmetric transfer characteristics of the back-gated bilayer graphene-FET before and after annealing. Before annealing, the device has a relatively low $I_{sd}$ with no significant Dirac point observed from $-30$ to $30$ V gate voltage. Here, the low $I_{sd}$ is limited by high contact resistances associated with the metal–graphene interface, where transfer-related polymer residues lead to a larger coupling length and reduce the coupling strength between the metal and graphene. In contrast, after annealing, it can be seen that the $I_{sd}$ of the device increases significantly where the Dirac point appears a positive $V_g$ of $16.1$ V, suggesting that predominant holes dominate the electrical transport of the bilayer graphene. It should also be noted that the Dirac point tends to shift to the higher $V_g$ when the $V_{sd}$ increases. This unusual shift of Dirac voltage is due to the change of carrier density distribution along the conducting channel as the $V_g$ varies. In addition, the $I_{sd}$ also increases with increasing negative $V_g$, indicating p-type doping of bilayer graphene. In this case, the water molecules are suspected to be the main dopant of p-type doping in the air during the measurement process under ambient conditions. The adsorbed water molecules that act as electron acceptors on the graphene surface and at the SiO$_2$–graphene interface would attract electrons from carbon atoms, thus generating major holes in the bilayer graphene.

The field-effect mobilities of electrons and holes were determined by estimating the linear plot of $I_{sd}$ versus $V_{g}$ curves using equation $\mu = (l/w)C_{ox}V_{sd}/(\Delta I_{sd}/\Delta V_{g})$, where $l$ and $w$ are the channel length and width, respectively, and $C_{ox}$ is the gate oxide capacitance per unit area (ca. $34.5$ nF cm$^{-2}$) for the $100$ nm thick SiO$_2$ layer. At a constant $V_{sd}$ of $1.0$ V, the field-effect mobilities of electrons and holes are $180$ and $410$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. It is noted that the carrier mobility values derived from this two-terminal FET device are lower than those of the sample measured by the Hall effect measurement because of the contribution of the contact resistance at the interface of the graphene, and the source–drain electrodes was not completely neglected here. Apart from that, the charge scatterings from the surface of the SiO$_2$ layer may also contribute to the low values of carrier mobility. However, this can be further improved by incorporating h-BN as a supporting layer during this direct CVD growth of bilayer graphene.

2.3. Large-Area Growth of Bilayer Graphene on Wafer. The bilayer graphene growth was also carried out on an $8$ in. wafer scale to demonstrate uniform growth capabilities over a large-area substrate. Figure 5a shows a photograph of the bilayer graphene grown on an $8$ in. Ni film/SiO$_2$/Si(100) wafer using a low-temperature CVD method as described earlier in the materials and method section. Using a vertical gas flow with appropriate gas ratios, the uniform bilayer graphene growth over the whole $8$ in. wafer area could be obtained in this work. Figure 5b shows Raman spectra scans performed along the radial direction starting from the center point ($a$) to the edge point ($h$) of the wafer. For the $I_{2D}/I_G$ ratio, a mean value of $1.15$ with a deviation of $0.14$ is achieved for the spot scans along the radial direction, comparable to the mean $I_{2D}/I_G$ ratio on the SiO$_2$/Si(100) substrate, indicating the predominant bilayer graphene domains despite having more defects near the edge of the wafer (indicated by the D band intensity). Meanwhile, a mean value of $0.47$ with a deviation of $0.13$ is obtained for the $I_{2D}/I_G$ ratio. To further examine the scalability of the growth process, the optical transmittance and sheet resistance of the graphene layers were measured at the corresponding spot scans. Before the measurements, the as-grown samples on the Ni films were directly transferred to a quartz substrate using a typical wet-chemical transfer method. Figure 5c shows plots of optical transmittance and sheet resistance as a function of radial distance. The optical transmittance of graphene layers along the radial distance after the transfer seems to vary with less than $5\%$ deviation in the optical transmittance at $550$ nm, indicating the good uniformity of the synthesized bilayer graphene. For instance, the mean value of the optical transmittance relatively increases from $94.94$ to $96.65\%$ with an increase in the radial distance due to the wide distribution of polycrystalline composed of single-layer and bilayer graphene. In parallel with the resultant optical transmittance, the mean value of the sheet resistance does exhibit a significant increase from $323$ to $664$ $\Omega$ sq$^{-1}$ with an increase in the radial direction, considering a possible increase in defects that were confirmed by the intensive D peak signal in the Raman spectra. This existence of defects may lead to the scattering of electron waves and change the electron trajectories, giving rise to higher resistivity in the graphene layers. At present, it is noted that the quality of graphene layers in this work is not as high as that of the thermal CVD process at high temperatures ($\sim$1000 °C) due to smaller in-plane crystallite sizes, which are estimated to be $28.3 \pm 10.2$ nm based on Tuinstra–Koenig relation. However, this drawback can be further elucidated by using high-cost single-crystalline metal substrates (e.g., single-crystal Ni(111)) or single-crystal Cu(111)) to prevent a possible abundance of defects on the interface boundaries. Furthermore, we also believe that the plasma source can be adopted for high-quality graphene growth via a diffusion-assisted synthesis method at much lower temperatures ($25$–$160$ °C), which would be a better route for integrated processing of graphene on the flexible devices fabricated at the front-end-of-the-line.

3. CONCLUSIONS

In summary, we demonstrated a practical method to produce large-area bilayer graphene on a polycrystalline Ni film using a liquid C$_6$H$_{12}$ precursor in a cold-wall CVD system at a temperature as low as $400$ °C. The morphology and structural properties of the bilayer graphene were successfully characterized by FESEM, AFM, HR-TEM, SAED, and Raman spectroscopy, showing that the coverage of the graphene layer is mostly bilayer with Bernal-stacking configuration. For the transport of bilayer graphene, the relation between temperature and resistance ($dR/dT < 0$) indicates its semiconducting behavior with predominant p-type doping, which is further supported by the back-gated field-effect transistor studies. The extracted Hall mobility from Hall effect measurements reached up to $710$ cm$^2$ V$^{-1}$ s$^{-1}$ with a low average sheet resistance of $370$ $\Omega$ sq$^{-1}$. The growth of bilayer graphene under local vertical gas flow was further demonstrated on an $8$ in. wafer-scale substrate and showed good film uniformity based on the sheet resistance and transparency measurements. To the best
of our knowledge, this low-temperature bilayer graphene growth by cold-wall CVD suggests a promising route for rapid growth, cost-effective, and wafer-scalable methods toward the development of large-scale graphene–Si heterogeneous nanoelectronics.

4. EXPERIMENTAL SECTION

4.1. Bilayer Graphene Growth from Liquid Benzene Source. Large-area bilayer graphene was grown from liquid benzene (C₆H₆) source (≥99.9%, Sigma-Aldrich) onto supported Ni film via a CVD method in an Oxford Plasmalab System 100. At first, the 150 nm-thick Ni film (99.99%, Kurt J. Lesker) was prepared on the SiO₂/Si(100) substrate by a radio frequency magnetron sputtering system, Edwards TF-600, at a base pressure of 2.0 × 10⁻⁶ bar at room temperature. As shown in the photograph and schematic of the CVD system (see Figure 6a,c), it consists of a load lock and a reaction chamber. The as-deposited Ni film/SiO₂/Si(100) substrate was manually loaded into the load lock and automatically transferred into the reaction chamber under a high-vacuum atmosphere of 0.02 Pa to ensure no residual oxygen impurities. Prior to the bilayer graphene growth, the surface of the Ni film was initially cleaned at 700 °C in a 100 sccm H₂ flow for 60 min and cooled down to the desired growth temperature (400, 300, 200, 100, and 25 °C, respectively). After the Ni pretreatment, the liquid benzene source that was kept in a bubbler at room temperature (see Figure 6b) was transported into the reaction chamber with a 3 sccm purified Ar flow (99.999999%) as carrier gas while another 250 sccm purified Ar flow (99.999999%) was transported separately for further dilution. The typical growth time was about 30 min at a pressure of 133.3 Pa. After completion of the growth, the as-grown bilayer graphene was automatically transferred to the load lock in a few seconds for rapid cooling to room temperature under a vacuum atmosphere of 0.133 Pa. The overall processes to grow bilayer graphene in this work are illustrated by schematic diagram in Figure 6d,e.

4.2. Bilayer Graphene Transfer Process. The bilayer graphene synthesized on the Ni film was transferred on the SiO₂/Si(100) quartz substrate and a lacey carbon-coated Cu grid by using a typical wet etching for further characterization. The transfer was initiated with a spin-coating of 100 nm-thick poly(methyl methacrylate) (PMMA) on the as-grown bilayer graphene (10 mm × 10 mm), followed by curing the samples at 80 °C on a hot plate for 5 min and immersing the whole samples in 0.1 M ferric chloride (FeCl₃) for a sufficiently long time to remove the Ni film. The resultant bilayer graphene with PMMA in the form of a transparent film was transferred in the deionized water to clean the Ni residues and the FeCl₃ etching agents. Then, the transparent film was transferred to the target substrate, where the remaining PMMA was removed in acetone to form the bilayer graphene.

4.3. Sample Characterization. The structural properties of the as-grown and as-transferred bilayer graphene were...
characterized by a confocal Raman imaging system (WITec, Alpha-300 R). The morphologies of the bilayer graphene were characterized by an optical microscopy system (Zeiss, LSM800), a field emission scanning electron microscopy (FESEM) system (JEOL, JSM-7500 F) operated at an accelerating voltage of 2.0 kV, a HR-TEM system (JEOL, JEM-2100) operated at an accelerating voltage of 200 kV, and an atomic force microscopy (AFM) system in the semicontact mode (NTEGRA Spectra, MT-MDT). Before HR-TEM imaging, the bilayer graphene was transferred on a lacy carbon-coated Cu grid using a wet-chemical transfer method. The SAED pattern for the sample was also taken on both thin and thick regions of the graphene layers during HR-TEM characterization. For the HR-TEM cross-sectional imaging of the bilayer graphene, a 90 nm thick lamella structure was first extracted from the surface through the thickness of the sample using a lift-out technique in a dual-beam system (FEI, Helios Nanolab 650) and further thinned with a focused ion beam (FIB) technique. For catalyst analysis, an X-ray diffraction (XRD) system (Bruker, D8 ADVANCE) was used to characterize the crystallinity of Ni film after the annealing and growth process. The purity of the as-grown and as-transferred bilayer graphene was further investigated by an X-ray photoelectron spectroscopy (XPS) system (Scanning XPS Microprobe, PHI Quantera II). The XPS system was operated under the conditions of the maximum electron kinetic energy of 1000 eV with 0.1 eV kinetic energy steps for a narrow scan. Note that the XPS spectrometer was calibrated using a clean polycrystalline Au foil, and a narrow scan of the Au 4f7/2 and Au 4f5/2 peak position was found at 84.0 ± 0.1 and 88.0 ± 0.1 eV, respectively. Therefore, all of the measured binding energies (BE) for the C 1s peak were accurate on an absolute scale within 0.1–0.2 eV. The optical transmittance measurements of the as-transferred bilayer graphene were characterized by a UV–vis spectrometer system (Agilent, Cary 7000). A blank quartz substrate was used as a reference for subtraction. For the electrical measurements, a Hall effect measurement system (Ecopia, HMS-5300) was used to characterize the transferred bilayer graphene. Subsequent contacts were first made by soldering indium dots of ∼0.5 mm size on each edge of the sample to allow the four-probe van der Pauw method. Next, the back-gated field-effect transistor (FET) by using the bilayer graphene was characterized using a source measure unit (SMU) system (Keithley 236) in the air at room temperature.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00841.

HR-TEM and FFT images of the graphene layers at different growth temperatures; Raman spectroscopy measurement of the as-grown graphene layers at high-temperature regimes; optical micrographs the graphene layers at different Ni film thicknesses; and comparison of XPS spectra of the as-grown and as-transferred bilayer graphene; and HR-TEM images of the multilayer graphene patch (PDF)

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Author Contributions

M.A.S.M. directed the project and wrote the main article text. The growth and characterization of graphene layers were conducted by M.A.S.M. and N.H.Z.A.; P.C.O., M.F.M.R., M.A.M., A.A.H., M.I.S., and A.M.H. provided support in the verification and interpretation of the results. All of the authors reviewed and approved the final version of the article.

Notes

The authors declare no competing financial interest.

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