

Seeded Growth of Ultrathin Carbon Films Directly onto Silicon Substrates

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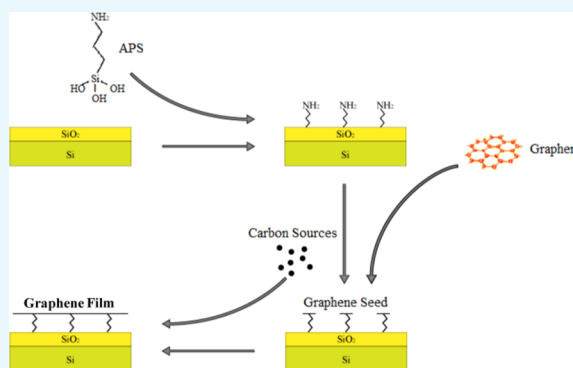
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ABSTRACT: The production of graphene films is of importance for the large-scale application of graphene-based materials; however, there is still a lack of an efficient and effective approach to synthesize graphene films directly on dielectric substrates. Here, we report the controlled growth of ultrathin carbon films, which have a similar structure to graphene, directly on silicon substrates in a process of seeded chemical vapor deposition (CVD). Crystalline silicon with a thermally grown 300 nm oxide layer was first treated with 3-trimethoxysilyl-1-propanamine (APS), which was used as an anchor point for the covalent deposition of small graphene flakes, obtained from graphite using the Hummers' method. Surface coverage of these flakes on the silicon substrate was estimated by scanning electron microscopy (SEM) to be around only 0.01% of the total area. By treating the covalently deposited graphene as seeds for CVD growth, the coverage was increased to >40% when using ethanol as the carbon source. Examination of the carbon thin films with SEM, X-ray photoelectron spectroscopy, and Raman spectroscopy indicated that they consist of domains of coherent, single-layer graphene produced by the coalescence of the expanding graphene islands. This approach potentially lends itself to the production of high-quality graphene films that may be suitable for device fabrication.



1. INTRODUCTION

Graphene¹ is an allotrope of carbon² that consists of a single layer of carbon atoms arranged in a covalently bonded hexagonal lattice.³ Among many reported properties, it has the potential to replace silicon in electronic devices^{4,5} and act as the core of next generation of logic circuits.⁶ However, there are still significant technological barriers to overcome to permit the large-scale application of this relatively newly “discovered” material.⁷ Although there are several approaches to overcoming the hurdle of effectively synthesizing graphene at a relatively large scale,^{8–10} none is totally appropriate for industrial production of quality graphene films.

Chemical vapor deposition (CVD)¹¹ is widely used in the semiconductor industry^{12,13} to produce high-performance solid-state materials such as silicon¹⁴ and is also seen as a potential method to produce graphene. To date, graphene films have been grown using CVD by passing hydrocarbon feedstocks over metal substrates¹⁵ such as copper, platinum, or gold. Here, the metal acts as a substrate as well as a catalyst,¹⁶ seeding carbon film growth. For this to occur, a hydrocarbon feedstock is fed over the heated metal substrate under vacuum or in a reducing H₂-rich atmosphere (Figure 1). The affinity between the carbon atoms and the metal is higher than that of other heteroatoms present,¹⁷ resulting in the decomposition of the feedstock and formation of metal carbide islands on the

surface of the metal. Upon recrystallization and surface reconstruction, these islands can form graphene sheets.

The main disadvantage of this CVD approach is that the graphene produced on the metal must then be transferred to another suitable substrate,¹⁹ for example, silicon, to be used in electronic devices or even to undergo further modification. This can lead to the introduction of defects into the film during the transfer process.²⁰ Here, we have used a metal-free CVD approach to grow graphene-like ultrathin carbon films directly onto modified monocrystalline silicon wafers²¹ by initially laying down a chemical tether on the surface. To this end, we bonded small fragments of graphene, of the order of several nanometers, obtained from bulk graphite using the Hummers' exfoliation method. These then act as nucleation sites, or seeds, for carbon film growth under CVD conditions in the complete absence of any metallic substrate or catalyst.

3-Trimethoxysilyl-1-propanamine (APS)²² has previously been used to add amine (–NH₂) terminations to glass

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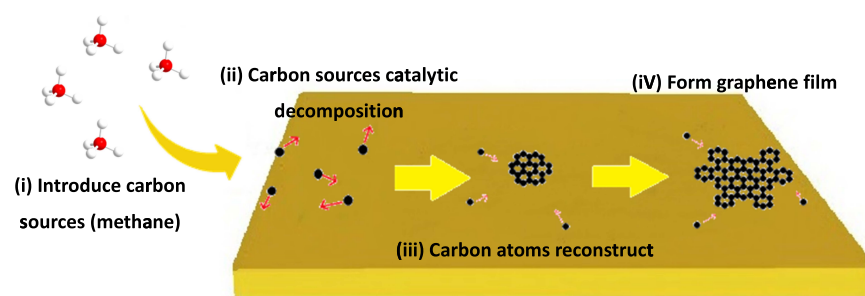
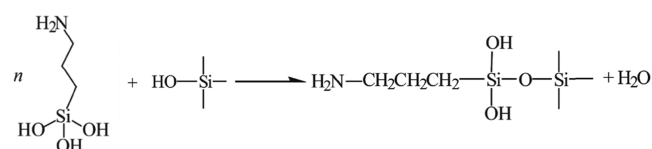


Figure 1. Schematic of a standard CVD experimental setup. Adapted with permission from ref 18 [Copyright 2015, Elsevier].

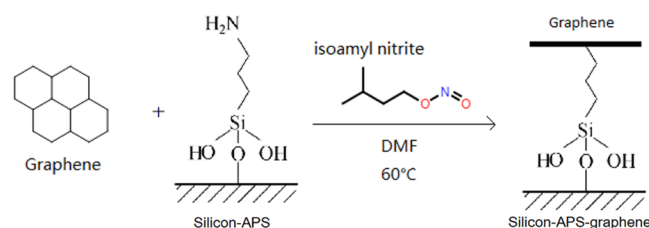
surfaces and is widely used in the fixing of DNA onto glass (Scheme 1). Applying this chemistry to an atomically flat, 300 nm SiO₂ layer on a Si wafer, the amine functionality can be effectively tethered to the surface of the Si.

Scheme 1. Reaction of APS and Silicon Dioxide



A well-known reaction, originally developed for carbon nanotubes, the so-called Tour reaction,²³ in which aniline derivatives are reacted with isoamyl nitrite to form an aryl diazonium intermediate, giving rise to radical addition of phenyl groups to the carbon surface, in this case graphene, is shown in Scheme 2. This was used to ensure seeding of the Si

Scheme 2. Graphene Fixed Process via APS on Monocrystalline Silicon



substrate only to areas where APS had been previously deposited, with no possible covalent addition elsewhere. Growth of carbon films by CVD from these seeds was subsequently achieved.

Using this approach, we have produced graphene-like ultrathin carbon films in a metal-free CVD method that is easy to achieve with low cost and broad applicability. Atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy were used to characterize the carbon films, indicating that this method has the potential to synthesize large-scale graphene films on silicon wafers, or using a similar principle, on a variety of substrates.

2. EXPERIMENTAL SECTION

All chemicals were obtained from Sigma-Aldrich and were used without further purification. Deionized (DI) water was used throughout the syntheses.

2.1. Graphene Powder Synthesis. Throughout this paper, the graphene (reduced graphene oxide) used was in powder form and was produced by a modified Hummers' method,²⁴ which uses strong oxidants to insert guest molecules and/or ions, i.e., "oxygen-containing functional groups" having negative charges, between the graphite layers to overcome the van der Waals' forces existing between layers.

Initially, concentrated sulfuric acid (96%, 23 mL, 0.415 mol) was added to graphite powder (1 g, 0.083 mol), followed by potassium permanganate (4 g, 0.025 mol). The reaction temperature was maintained below 4 °C and the solution was agitated for 2 h to make sure that the reactants had mixed homogeneously. Then the reaction temperature was increased to, and maintained at, 40 °C while stirring for half an hour; during this stage, the graphite sheets underwent oxidation. DI water (50 mL) was then added to the reaction solution, and the reaction temperature was further increased to 95 °C. During this stage, the aqueous species intercalated between different graphite layers, sharply increasing the interplanar distance. The final product was washed several times (usually four–five times) using DI water by centrifugation, until the supernatant liquid was totally transparent. The supernatant liquid was then removed, leaving multilayered graphene oxide as a solid. This was dried in a vacuum drying oven for 12 h (at 95 °C, under dynamic vacuum) prior to further experiments.

2.2. Modification of Monocrystalline Si/SiO₂ by APS.

A 300 nm SiO₂ layer was grown on a polished p-type monocrystalline Czochralski silicon wafer using the thermal oxidation method.²¹ The surface was then cleaned in an ultrasonic bath for 15 min using DI water and left to dry for 2 h in a vacuum furnace (at 95 °C, dynamic vacuum). The washed Si was then bathed in a 4% APS solution (2 mL, 0.011 mol) in acetone (50 mL, 0.666 mol) at room temperature for 4 min. It should be noted that to get a high density of graphene seeds, relatively high concentrations of APS were typically used over long reaction times.²²

2.3. Attachment of Graphene Seeds onto Modified Si.

The Si wafer modified with APS was carefully placed at the bottom of a glass reaction flask to which a dispersion of 50 mg (about 0.004 mol) of graphene (oxide) powder and 2.2 mL of isoamyl nitrite (0.016 mol) in 20 mL of dimethylformamide (DMF) (0.242 mol) was added. The reaction mixture was then heated in an oil bath at 80 °C using a reflux condenser and with continuous stirring for 12 h.

2.4. Production of Ultrathin Carbon Films Using CVD.

The Si wafer to which the APS and graphene seeds were attached was then cleaned in an ultrasonic bath for 15 min using ethanol (98%) and left to dry for 2 h in a vacuum furnace (at 95 °C, vacuum drying). To avoid breaking of the chemical bonds between the graphene seeds and silicon wafer, which

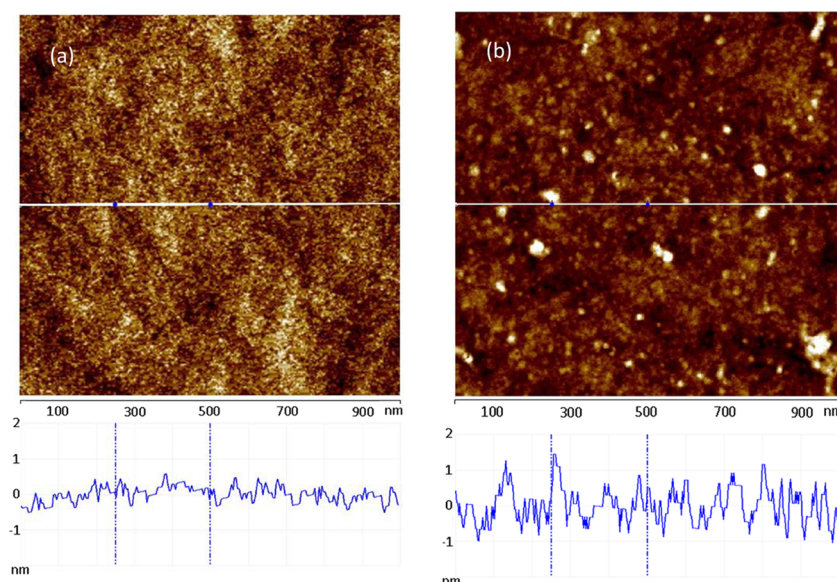


Figure 2. AFM images showing (a) the surface of the raw Si wafer complete with the 300 nm SiO₂ layer and (b) the same surface post treatment with APS-tethered graphene flakes.

could cause the seeds being removed from the substrate, a low powered Ultrasonic Cleaner (FXP 10N, produced by Unisonics) was used.

The clean Si wafer with tethered graphene flakes was placed into the CVD reaction chamber with the graphene face exposed and heated to 800 °C with an ethanol reservoir used as the carbon source. At these elevated temperatures (above ca. 750 °C), the ethanol vapor undergoes dehydration to decompose into ethylene.²⁵ The pressure in the reaction chamber was maintained at about 1 kPa by dynamic vacuum. In previous studies of graphene growth on metal substrates from an ethanol feedstock, growth temperatures have ranged between 850²⁶ and 900 °C.²⁷ Thin carbon films have previously been grown on metal-free substrates at a high concentration of the carbon source.²⁸ However, this approach leads to significant deviation from planar graphene structures as the nucleation process readily occurs on the surface of previously deposited carbon layers, eventually leading to bowl-shaped products. By selecting to use lower CVD reaction pressures, we aimed to ensure that the graphene seeds acted as templates and nucleation sites for the crystallization of deposited carbon atoms preferentially at the edge sites.

A limitation of our use of ethanol as the carbon source is the limited reaction time due to the fact that the ethanol reservoir would run dry in around 15 min (by closing off the dynamic vacuum, the remaining ethanol vapor could be used to extend the reaction time to half an hour). This is due to the design of the reaction chamber, which restricted the refilling of ethanol during the experimental process; extended growth times therefore required repeating the CVD experiment several times.

An alternate carbon source, methane, was also used to further assess the role of the CVD conditions. In this case, the Si wafer with tethered graphene flakes was placed into the CVD reaction chamber with the graphene face exposed and 30 sccm of methane flow was introduced into the chamber at temperatures up to 950 °C. These conditions were held stable over the prescribed CVD processing time, after which the sample was annealed for 1 h to release the residual stress

(initially maintained at 950 °C for 0.5 h, then decreased to 475 °C at a cooling rate of 10 °C/min, and finally maintained for 0.5 h, all with a flow of 30 sccm H₂).

2.5. Sample Characterization. Atomic force microscopy (AFM) was performed in contact mode using an ICON SPM, produced by the Bruker Company with a 512 point scan line. Scanning electron microscopy (SEM) images were obtained using a NanoSEM 450, produced by the FEI Company, under a 5 kV accelerating voltage. Raman spectra were measured on a Renishaw inVia spectrometer, with 532 nm laser excitation. Finally, X-ray photoelectron spectra (XPS) were obtained on a Thermo Scientific ESCALAB 250Xi, with a monochromated Al K α X-ray source ($h\nu = 1486.68$ eV) and at 100 eV for survey scans.

3. RESULTS AND DISCUSSION

3.1. Graphene Seeds Tethered onto Modified Monocrystalline Silicon. AFM images of the Si wafer before and after the addition of graphene shown in Figure 2 clearly show the near atomically flat SiO₂ surface prior to decoration with graphene (Figure 2a). The graphene flakes used as seeds in subsequent CVD film growth can be clearly seen in Figure 2b; the size across the seed flakes was found to be 50–100 nm, with a height of 1–1.5 nm, as determined by measuring the trajectory across the SiO₂ surface. This is fully consistent with the graphene particles being chemically fixed onto the surface of the silicon wafer.

3.2. Seeded Growth of Ultrathin Carbon Films Using CVD with Ethanol as the Carbon Source. The surface of Si decorated with graphene seeds was investigated using XPS (Figure 3). For graphene and reduced graphene oxide, there are three characteristic XPS C1s peaks in the XPS C1s spectrogram²⁹ located at 284.5 eV (C–C), 286.4 eV (C–O), and 287.8 eV (C=O). This provides an estimation of the oxygen content of the samples based on the ratio of C–C and C–O or C=O. As can be seen in Figure 3, the result of graphene fixed on silicon and 4.0 h of CVD growth (with ethanol as the carbon source) shows peaks that are typically characteristic of graphene with a low oxygen content.

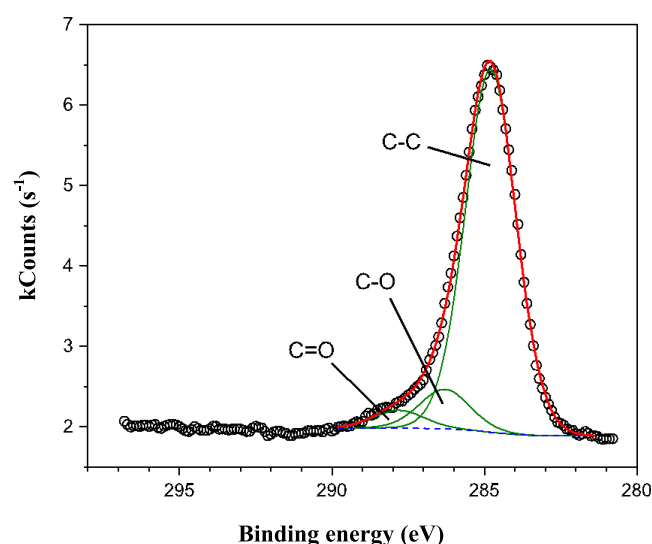


Figure 3. XPS C 1s peak of silicon-APS-graphene after 4.0 h CVD growth with fitting; the red solid line is the sum of the individual fits in green on top of a background shown by the blue dashed line.

Analysis of the atomic percentage of carbon from the XPS data (Table 1), provides the variation in carbon content on the

Table 1. Atomic Percentage of Carbon on the Decorated Si Surface at Different Stages of CVD Treatment

	284.5 eV (C-C) (%)	286.4 eV (C-O) (%)	287.8 eV (C=O)
silicon wafer with 300 nm SiO ₂ layers	5.30	0.69	0.21%
APS decorated silicon wafer	6.20	0.51	N/A
graphene decorated silicon wafer after the 0.5 h CVD process	6.11	2.93	0.56%
graphene decorated silicon wafer after the 4.0 h CVD process	11.17	1.22	0.55%

decorated Si surface. It can be seen that the content of carbon atoms in C-C bonds on the surface increased after both linking the graphene seeds with APS and the subsequent CVD processing. Of note is that the decorated Si wafer had a greater content of C-O bonds after only 0.5 h of CVD than after 4.0 h. This reflects the fact that the seeds bound to the Si by the APS tethers are reduced graphene oxide, produced by the Hummers' method, and as such contain more C-O bonds than pure graphene-like films. After extended CVD processing times, the "graphene seeds" grew to larger graphene-like carbon films as opposed to graphene oxide, thus decreasing the relative atomic percentage of C in C-O bonds.

Comparing the AFM images of Si decorated with graphene seeds (Figure 4a) and the same sample after 0.5 h of CVD with ethanol as the carbon source (Figure 4b), it is clear that the size of the individual graphene seeds increased, even after only 0.5 h of CVD processing; however, the growth is not very extensive at this stage. It should be noted that the average thickness of graphene flakes also decreased to about 1–2 nm upon CVD treatment, assumed to be due to the high temperatures that overcame the van der Waals' forces between graphene layers, removing those extra layers not directly fixed onto the substrate. Evidence of this phenomenon was also found in the Raman spectroscopy studies.

In contrast, the AFM image shown in Figure 4c for the Si wafer without graphene seeds and after 5.0 h of CVD processing shows a surface that is still very flat and similar to raw Si, indicating that without the graphene seeds in place, carbon atoms do not deposit on the surface of silicon and no film growth is observed.

Figure 5 shows the SEM images of Si decorated with graphene seeds after CVD processing times of between 0.5 and 9.5 h (with ethanol as the carbon source). It is clear that as the reaction time increases, the size of the carbon islands also increases, to the point that after 9.5 h of CVD, the films cover almost half of the surface area.

By discriminating between the dark and light regions and analyzing the ratio of pixels, it was determined that after 9.5 h of ethanol-CVD, the percentage coverage of graphene rose from initially under 0.01–37.1(5)%. Analysis of the SEM images of the graphene films grown from seeds attached to the Si wafer at different CVD reaction times gives an approximate growth profile (Figure 6). This highlights the near-exponential growth rate of the graphene seeds over the CVD reaction times studied, resulting in around 40% coverage after almost 10 h. This growth profile extrapolates to a Boltzmann growth model centered at 11.3(58) h, highlighting the fact that the growth rate has a Gaussian profile (Figure 6, inset), with the initial nucleation points growing in number as the edge sites increase, before coalescence of seeds leading to a slowing of growth, with near complete coverage at around 24 h. In addition, after 9.5 h of CVD processing, notably sharp-edged carbon islands had formed, indicative of graphene-like regions within the ultrathin carbon films.

To further assess the nature of the carbon film attached to the Si substrate, Raman spectra were recorded after various elapsed CVD times. The Raman spectrum of graphene primarily consists of bands labeled in the literature as the G, D, and G' bands. The G band lies around 1585 cm⁻¹ and is the major characteristic feature of graphene; it is due to in-plane motions of the carbon atoms. As the number of layers increases, the G band position has been reported to shift to lower frequencies, following a $11/(1+n^{1.6})$ dependence, where n is the number of layers.³⁰ The D band is usually considered as a disorder band and is found around 1350 cm⁻¹. The intensity ratio of the D and G bands (I_D/I_G) is a useful measure of the extent of defects or edge sites of a graphene sheet.³¹ The G' band, also called the 2D band, usually lies around 2700 cm⁻¹ and is a second-order two-phonon process; it exhibits an unusually strong frequency dependence on the excitation laser due to a double resonance process that links the phonon wave vector to the electronic band structure.³² The intensity of the G' band ($I_{G'}$) can also be used to indicate the number of graphene layers; for perfect single-layer graphene, $I_{G'}$ is larger than I_G , while with increasing number of layers, $I_{G'}/I_G$ decreases dramatically. The position of G' also shows a blue shift as a function of the increasing number of layers.³³

Comparing the Raman results (Figure 7), it can be seen that before CVD, there is no peak typical of carbon films of any kind; this reflects that the density of the seeds fixed to the substrate is too small to generate an appreciable Raman signal (the band at ~1450 cm⁻¹ is assigned as the third-order silicon TO phonon, while the narrow transition at ~2330 cm⁻¹ arises from atmospheric nitrogen gas). When ethanol was used as the carbon source, graphene-like Raman peaks arose and with increased CVD processing times, the position of the G band

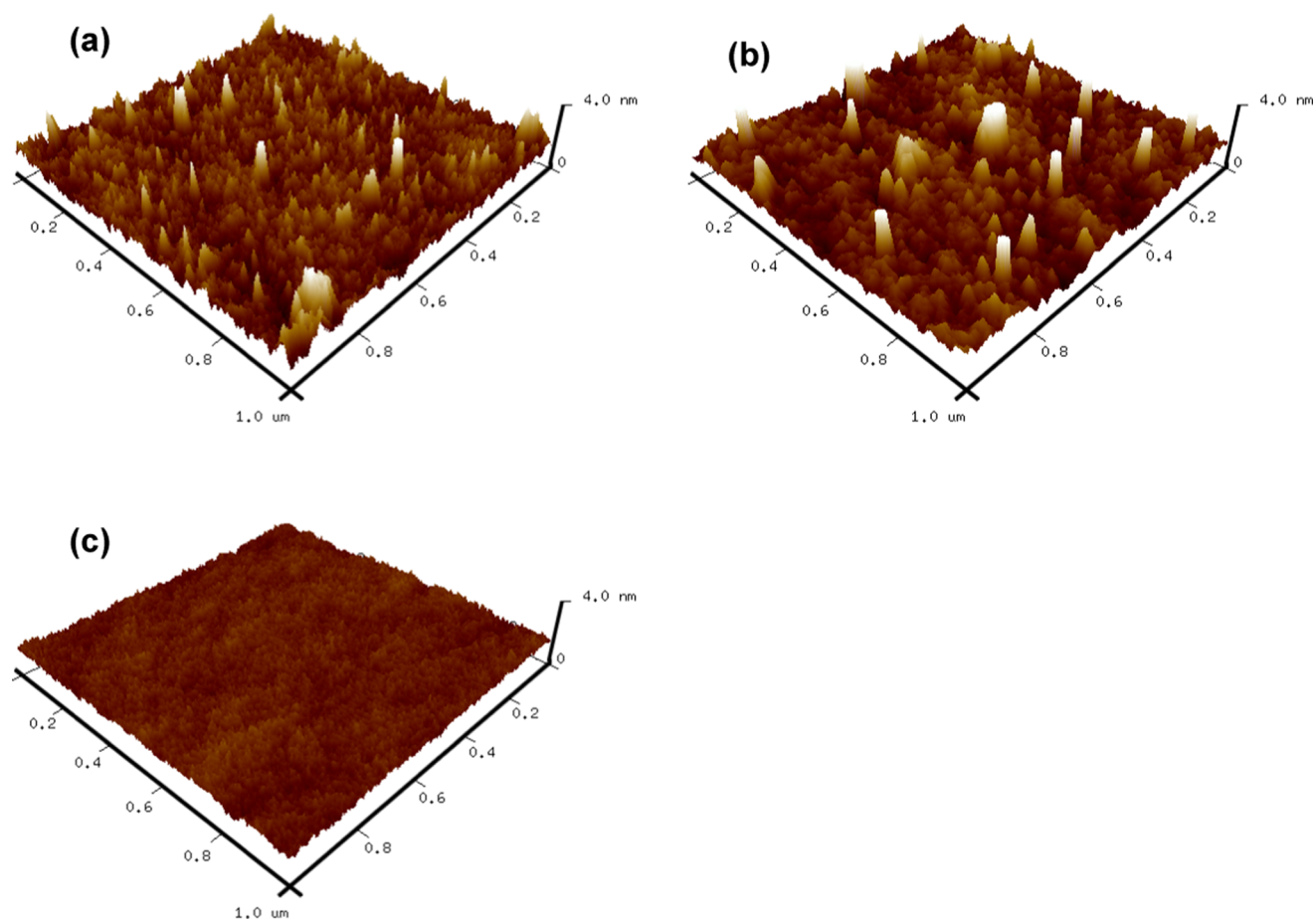


Figure 4. AFM images showing (a) the surface of the raw Si wafer complete with the 300 nm SiO₂ layer and post treatment with APS-tethered graphene flakes and (b) the same surface after the 0.5 h CVD process. (c) Si wafer complete with the 300 nm SiO₂ layer and after the 5.0 h CVD process.

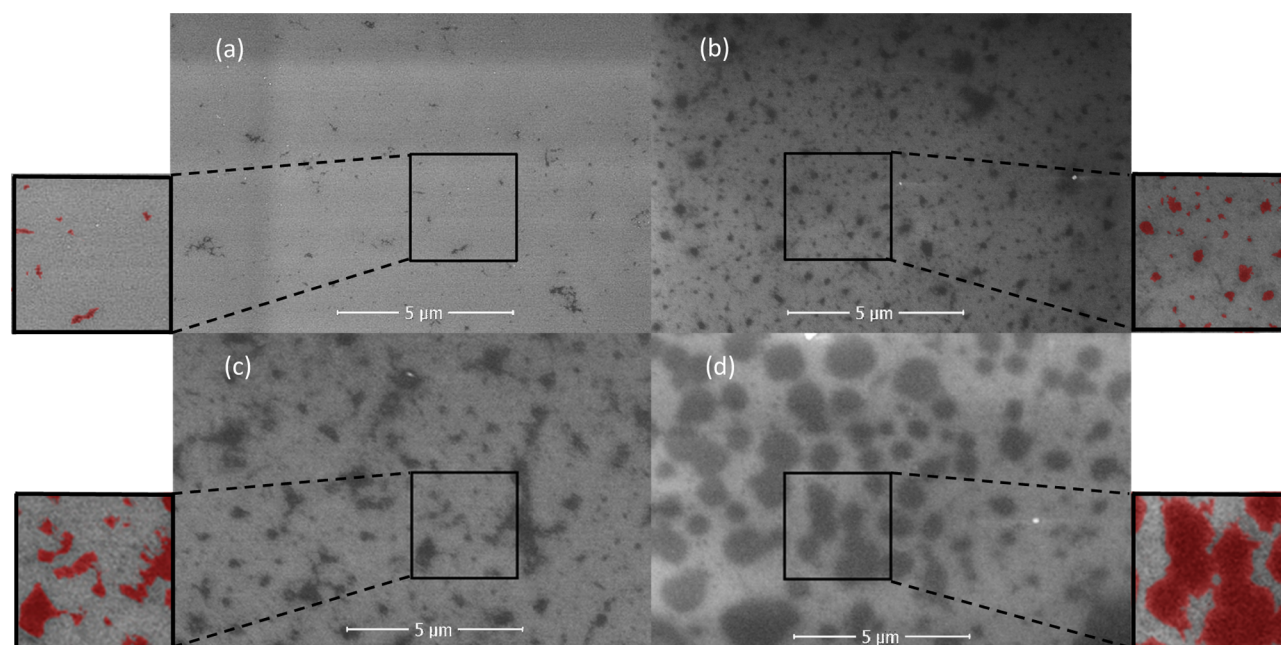


Figure 5. SEM images showing the surface of the raw Si wafer complete with the 200 nm SiO₂ layer and post treatment with APS-tethered graphene flakes and (a) after the 0.5 h CVD process; (b) after the 5.0 h CVD process; (c) after the 8.0 h CVD process; and (d) after the 9.5 h CVD process with ethanol steam as the carbon source.

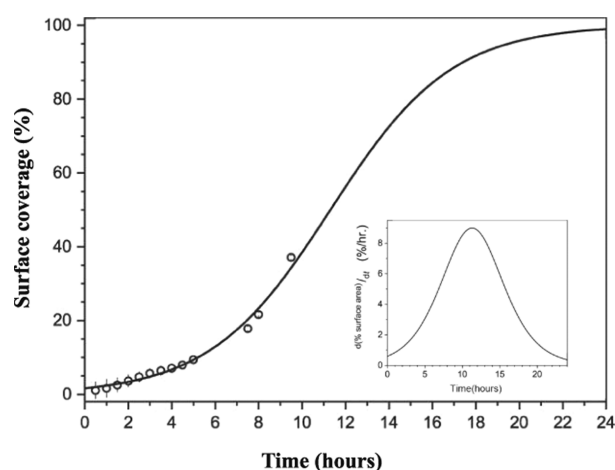


Figure 6. Boltzmann growth profile of seeded graphene on Si wafers expressed as percentage of coverage of carbon films at different CVD growth times; $R^2 = 0.982$. Inset: Idealized Gaussian profile of the growth rate as a function of time.

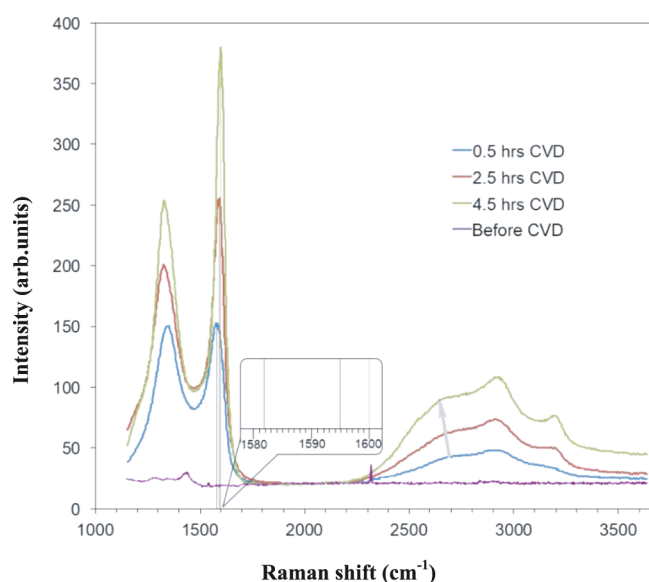


Figure 7. Raman spectroscopy results using a 532 nm laser: decorated Si with graphene seeds before and after the 0.5–4.5 h CVD processes; and the silicon wafer modified by APS.

shifted to higher frequencies and the G' band underwent a red shift; in addition, I_D/I_G also decreased with the reaction time. This demonstrated that after CVD processing, not only had the graphene seeds undergone growth but the quality of the sheets had also increased. This was largely due to the extra layers in the reduced graphene oxide seeds that were initially deposited on the APS–Si being removed at high temperatures, while defects in the graphene seed also underwent repair by incorporating carbon atoms during the CVD process.

3.3. Seeded Growth of Graphene-like Carbon Films Using Methane as the CVD Carbon Source. Methane is a more commonly used carbon source than ethanol in the CVD production of graphene or carbon films. In our seeded growth of carbon films, using methane as the carbon source could significantly increase the rate of film growth over ethanol during the CVD process. Figure 8 shows the Raman spectra of decorated Si–APS with graphene seeds after 2 and 4 h of methane-CVD processing. It is immediately apparent that at

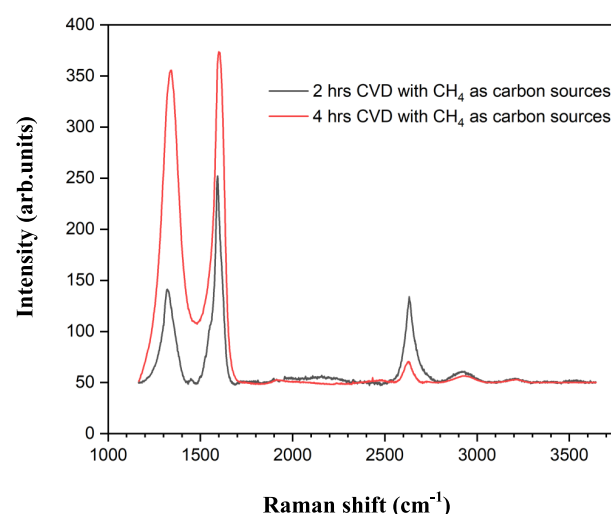


Figure 8. Raman spectroscopy results using a 532 nm laser: decorated Si with graphene seeds after the 2.0 and 4.0 h CVD processes with methane as the carbon source.

short growth times (2 h), the carbon film shows more graphene-like peak characteristics than that produced with ethanol as the carbon source. The G' band of the methane-sourced film is much clearer and has a higher intensity ratio $I_{G'}/I_G$, which is close to that typical for a graphene material of four layers. However, when the growth time was extended to 4 h, the film was found to have graphitized. We speculate that this is because the methane carbon source more readily undergoes decomposition to carbon atoms relative to ethanol. Initially, this aids the repair of damage or vacancy defects of the graphene seeds, enhancing the graphene-like properties, but with extended growth times, the high concentration of carbon atoms results in deposition not only on the edges of the expanding graphene seeds but also on the surface of the graphene film. This then initiates another nucleation process, which is repeated during CVD processing, resulting in more graphene layers than the original graphene seeds.

Comparison of Figure 5 and 9 highlights differences in the SEM images of graphene-like carbon films produced from methane (Figure 9) and ethanol (Figure 5) as carbon sources. This is consistent with the idea that methane-CVD results in faster growth of the graphene seeds than ethanol-CVD. At 2.0 h of CVD growth (Figure 9a), the average size of the carbon films produced under methane is greater than that after 5.0 h of ethanol-CVD (Figure 5b). However, after 4.0 h of methane-CVD growth, a loss of overall control of the deposition was observed, leading to the transformation of the film from a two-dimensional material into three-dimensional crystalline (graphitic) objects (Figure 9b).

4. CONCLUSIONS

Graphene has great potential across a number of fields; however, there remains much work to be done before it can be used in large-scale applications, with the biggest problem being a stable production method. This work aimed to develop a new method of producing high-quality graphene films. The results show that the properties of carbon films produced directly on a Si substrate are similar to those of graphene and that the film size extends to more than $10 \mu\text{m}^2$.

The main advantage of this method is the fact that it uses a metal-free substrate and produces graphene-like carbon films

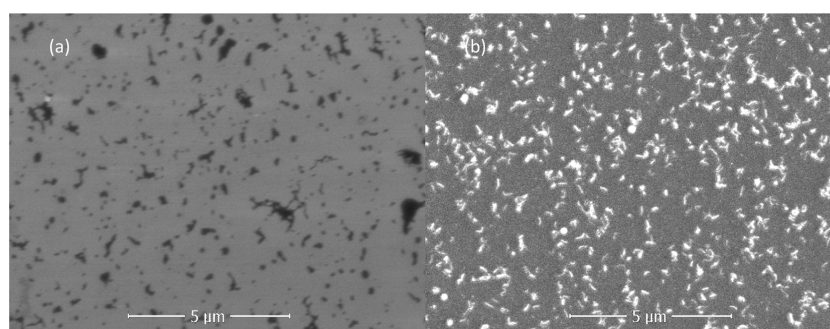


Figure 9. SEM images showing the surface of the raw Si wafer complete with the 200 nm SiO₂ layer and post treatment with APS-tethered graphene flakes and (a) after the 2.0 h CVD process and (b) after the 4.0 h CVD process with methane as the carbon source.

directly on Si, avoiding the need for additional processing to transfer the film, that can lead to defects and impurities in the films. Compared to other metal-free CVD graphene production methods, this new approach is relatively easy and with few steps,³⁴ retaining the structural form of the final films post growth²⁸ and do not require further processing.³⁵ While methane as a CVD feedstock was found to yield carbon films more akin to graphene, film growth was more difficult to control due to the rapid reaction relative to that of ethanol. Rapid film growth was found to result in a tendency to undergo graphitization upon prolonged (>2 h) CVD processing.

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Author Contributions

Z.Y. prepared and characterized all samples and prepared the initial draft of the manuscript; R.J. and Y.Y. provided access to the CVD apparatus and guidance therein; G.P. provided the atomically flat SiO₂-coated Si wafers; J.A.S. oversaw and directed the research project and completed extensive editing of the manuscript. All authors have contributed to the final manuscript.

Notes

The authors declare no competing financial interest.

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