Rapid epitaxy-free graphene synthesis on silicidated polycrystalline platinum

Vitaliy Babenko, Adrian T. Murdock, Antal A. Koós, Jude Britton, Alison Crossley, Philip Holdway, Jonathan Moffat, Jian Huang, Jack A. Alexander-Webber, Robin J. Nicholas & Nicole Grobert

Large-area synthesis of high-quality graphene by chemical vapour deposition on metallic substrates requires polishing or substrate grain enlargement followed by a lengthy growth period. Here we demonstrate a novel substrate processing method for facile synthesis of mm-sized, single-crystal graphene by coating polycrystalline platinum foils with a silicon-containing film. The film reacts with platinum on heating, resulting in the formation of a liquid platinum silicide layer that screens the platinum lattice and fills topographic defects. This reduces the dependence on the surface properties of the catalytic substrate, improving the crystallinity, uniformity and size of graphene domains. At elevated temperatures growth rates of more than an order of magnitude higher (120 μm min⁻¹) than typically reported are achieved, allowing savings in costs for consumable materials, energy and time. This generic technique paves the way for using a whole new range of eutectic substrates for the large-area synthesis of 2D materials.
Graphene is a two-dimensional material that has great potential for use in a wide variety of applications such as transparent flexible electrodes, photonic and electronic devices, energy storage, sensors and coatings to name a few. Exceptional electrical, optical and mechanical properties of the material greatly depend on the quality of the synthesized graphene that can inherently depend on the underlying substrate. Notably, the production of large area, single crystal graphene with a controlled number of layers is a challenge that has yet to be resolved.

Atmospheric pressure chemical vapour deposition (APCVD) has received much attention due to its simplicity, improved safety and lower cost over alternative procedures. When a solid substrate is used with APCVD, graphene growth is strongly influenced by the crystallographic lattice of the substrate, its defects, roughness and grain boundaries. Millimetre-sized polycrystalline Pt foils with a silicon-containing film, which forms a wetting liquid silicide surface on silicidated Pt. For comparison, the window of useful H2 to CH4 ratios was 100:1. The ratio of H2 to CH4 on silicidated Pt compared with pristine Pt had to be increased by as much as 50% (1,150 °C) to reduce the carbon deposition and achieve flakes of comparable size to those on pristine Pt. The comparison of the synthesis parameters on pristine and silicidated Pt is presented in Supplementary Fig. 1. This meant that the quality of graphene flakes improved without sacrificing the short experimental time.

The difference in the kinetics for graphene nucleation and growth on pristine and silicidated Pt may be the key to explain this observation. Studies show that the bond strength of Si-C (~318 kJ mol⁻¹ (ref. 19)) is higher than that of Pt-C (~225 kJ mol⁻¹ (ref. 20)), but still lower than the graphene bond (~400 kJ mol⁻¹ (ref. 21)) presenting a 'stickier' silicide surface. This suggests that the associated dwell time of carbon atoms on the silicidated surface could be prolonged, leading to the observed increase in the growth rate.

Interestingly, the high melting point of Pt allowed us to probe unexplored temperatures above 1,100 °C in CVD, at which single crystal graphene flakes of up to 1.8 mm were obtained in 15 min on silicidated Pt. For comparison, the window of useful H2 to CH4 ratios on Cu is usually such that experiments often need to be conducted for hours or days to grow large-area, single crystal, monolayer graphene. Figure 1 depicts the improvement in the overall size of the flakes on the nm-scale that can be obtained with higher temperature on silicidated Pt. While graphene on pristine Pt showed similar trends, only smaller, polycrystalline flakes of irregular shape were observed throughout the CVD parameter space. The size of graphene flakes can be determined by multiplying the growth rate by the synthesis time with the nucleation point separation as the maximum achievable graphene average domain size. The dependence of the growth rate as a function of temperature for silicidated and pristine Pt substrates is shown in Fig. 1. As previously reported for Cu the nucleation density of the domains also decreased with higher temperatures. However, on Pt the flake size was approximately an order of magnitude larger for the same temperature and time. The domain size of hexagonal or irregularly shaped graphene grown on Cu, Pt and silicidated Pt is related as follows Cu (1,050 °C) < Pt (1,050 °C) < Pt (1,150 °C) < silicidated Pt (1,150 °C). The difference in the nucleation point separation between pristine Pt and silicidated Pt is not as significant as the difference in the
growth rate, yet it is still noticeable. The nucleation point separation (S), related to the nucleation density as $\pi^{-1}(S/2)^{-2}$, is also shown in Fig. 1e.

**Graphene characterization and electronic properties.** A number of techniques were used to extensively assess the properties of the synthesized graphene, such as size, shape, crystallinity, number of layers and its electronic properties. Figure 1c,f shows two characteristic scanning electron microscope (SEM) images of graphene flakes on silicidated Pt and on pristine Pt. The latter had many reflex angles that indicated numerous grain boundaries (Supplementary Fig. 2), and the edge morphology often varied from one Pt grain to another, similar to what has been reported by Sun et al. and Ping & Fuhrer. In contrast, the hexagonal graphene flakes of millimetre size grown on silicidated Pt were observed to cross sometimes hundreds of the Pt grains and their boundaries without any effect. Monolayer graphene was easily achieved on pristine Pt and silicidated Pt, most likely due to easily achieved ‘balance regime’ between surface catalysis and segregation. However, the crystallinity and size varied markedly depending on the experimental conditions. Contrary to the previous study of graphene synthesis on pristine Pt by Gao et al., where Pt was reused thousands of times inside a fused silica tube, we did not observe any hexagonal graphene flakes on pristine Pt that was not reused. The silicide surface is conductive and not easily distinguishable under an SEM, which may explain why the presence of silicides (Supplementary Fig. 3) has not been noticed and their striking influence on graphene growth in CVD has not been studied or reported before. The possibility to reuse Pt in combination with short experimental times can reduce costs and be reused.

Graphene was transferred to Si/SiO$_2$ substrates for Raman measurements (Fig. 2a). The D-peak was almost indistinguishable from the background indicating low defect concentration. The ratio of G’ to G peaks exceeded two over large areas, as expected for good quality monolayer graphene, both for hexagonal and irregularly shaped flakes. Large-area graphene was transferred to plain transmission electron microscopy (TEM) grids (Au, Agar) without amorphous carbon support. TEM images and selected area electron diffraction patterns (SAED) were recorded. A line profile of the SAED pattern (Fig. 2b) provided additional supporting evidence for monolayer graphene. The hexagonal shape of the flakes suggested good crystallinity, but to confirm this SAED patterns were recorded at points across large areas of a graphene flake on a TEM grid (Methods, Supplementary Fig. 2). In addition, lattice-resolution AFM scans of 6 nm × 6 nm were recorded on as-grown graphene on silicidated Pt and their Fourier transforms (FT) were taken (Fig. 2c). The roughness of the substrate after solidification was limiting the resolution of AFM images, but small-area scans were sufficiently flat and thus suitable for the FT analysis. These methods provided ways to measure the rotation of the lattice over distances of hundreds of micrometres. The measured values showed no significant changes in the rotation of the lattice and confirmed that the synthesized graphene was indeed a single crystal.

To assess the electronic properties of our CVD graphene a Hall-bar device (Fig. 2e) was fabricated from graphene transferred onto SiO$_2$/Si substrates (methods) from silicidated Pt. The carrier density $n$ and mobility $\mu$ of the device were determined from the low-field Hall measurements with $n = (e \cdot \partial \rho_{xx}/\partial B)^{-1}$ and $\mu = (en\rho_{xy})^{-1}$. Small p-type doping was observed in our device, which is also commonly seen in transferred graphene on SiO$_2$/Si substrates and considered to be due to the adsorption of water molecules between the interfaces. Figure 2d shows the $\rho_{xx}$ and $\rho_{xy}$ as functions of magnetic field from −19 to +19 T for a typical device. We observed a very high hole mobility of 5,525 cm$^2$/V$^{-1}$s$^{-1}$ at a hole density of $5.86 \times 10^{11}$ cm$^{-2}$. The Hall mobility $\mu_H$ was calculated from $\mu = \rho_{xx}/\rho_{xy}$.
Recently, graphene has been shown to be an exceptional candidate for quantum Hall metrology exhibiting the highest breakdown current density of any material. In our sample, at $|B| > 12$ T, well-defined $v = 2$ quantum Hall states were clearly observed with $\rho_{xy} = \frac{h}{2e^2}$ and $\rho_{xx} = 0$, consistent with its carrier density $\left(\frac{|B|_{v=2}}{4B}\right)$. These observations confirm the high quality of our monolayer graphene with good crystallinity, very low defects and impurities, and that graphene grown on silicidated platinum may be useful for quantum resistance metrology. The carrier mobilities obtained from the magnetotransport measurements are among the highest of reported values for CVD graphene on SiO$_2$/Si substrates, and are comparable to those in epitaxial graphene grown on SiC (ref. 29). Using more sophisticated transfer methods or substrates with less charged impurities, such as h-BN, further improvement of the carrier mobility is expected.

**Substrate characterization and silicidation mechanism.** It is commonly known that Pt is a noble metal that is very inert; only hot aqua regia can react with it. Silicon dioxide (SiO$_2$), fused silica or quartz may be described similarly due to the strong Si—O bond, which can be broken by hydrofluoric acid or some strong bases. However, when these compounds are in contact in a reducing H$_2$ atmosphere at elevated temperatures silica may reduce to silicon, catalysed by Pt, and react with Pt to form various phases of eutectic Pt silicides as reported by numerous studies. The two simplified reactions are:

\[
\text{SiO}_2 + 2 \cdot \text{H}_2 \rightarrow \text{Si} + 2 \cdot \text{H}_2\text{O} \quad (1)
\]

\[
x \cdot \text{Si} + y \cdot \text{Pt} \rightarrow \text{Pt}_x\text{Si}_y \quad (2)
\]

If pure silicon is deposited onto Pt, then the reaction proceeds much quicker and starts at lower temperatures. Other films, such as SiO, SiN also react in a similar manner. We found that a boron nitride holder was the most suitable for the Pt due to its stability in a reducing atmosphere and not-wetting by the silicide.

Characterization of the annealed and cooled substrate before graphene synthesis was performed. The cooling was rapid (quenched) to obtain the closest possible condition to that during the synthesis. Figure 3a,b shows an SEM image of a grain boundary of the substrate and its corresponding energy-dispersive X-ray (EDX) spectral map of the silicon peak. The grain boundary and the small topographic defect have higher silicon content compared with the surroundings. The silicon peak is very prominent (Fig. 3c) in such valleys, but is typically much lower, but often detectable on the Pt grains. The presence of a variety of ‘frosted’ features and striations in SEM also supported the formation of a thin silicide layer (Supplementary Fig. 3).

X-ray photoelectron spectroscopy (XPS) revealed that Pt silicide covered the entire substrate (see peak at around 100.5 eV (ref. 37); Fig. 3d). Additional SiO/SiO$_2$ peaks were also observed and are most likely formed when the silicide was exposed to air. Complimentary X-ray diffraction (XRD) analysis was performed to confirm the chemical composition, but also to identify the phase of the solidified silicide. For this, a thick SiO$_2$ (~3 μm) film was deposited on Pt to get the material in excess, resulting in the formation of a Pt$_3$Si phase that matched well with the literature (Fig. 3e), but possibly other phases were present under different synthesis conditions. Cross-sectional EDX maps were recorded on Pt foils with a varying thickness of the silica layer to better understand the Pt/silica reaction and the chemical composition in...
the bulk. After the sample was annealed and quenched, regions with a thin silica layer (≤500 nm) did not show a detectable silicon peak in the EDX maps (Fig. 4a). Regions with a higher initial silica thickness (>500 nm) showed a high silicon signal (Fig. 4b) around the grain boundaries, suggesting that the reaction proceeded faster in those areas while progressing slowly into the bulk of the grains. Finally, excess silica (≥3,000 nm) resulted in the restructuring and degradation of the foil due to the formation of a two-phase composite (Fig. 4c), held together by the silicon-containing compound.

On the basis of experimental observations of the SiO2 film before and after annealing we propose a simple mechanism of the liquid silicide formation that explains why the morphologies of graphene are so different on pristine and silicidated Pt. Most Pt silicide phases have reduced (eutectic) melting points40, especially in the form of a thin film. For example, the identified monoclinic Pt3Si phase melts at around 830°C (ref. 40). Figure 5 shows a diagram of our proposed silicide formation mechanism and the corresponding SEM images of the Pt/SiO2 stack. The deposited silica layer is not conductive and appears dark under the electron beam. Upon heating, a spontaneous reaction occurs at a variety of points in the film that start to spread in a circular manner. We believe the circular holes in the silica film are filled with a thin layer of a conductive liquid, which when cooled appear similar to the pristine Pt but with a 'frosted' surface (Fig. 5b,c, Supplementary Fig. 3). The silicide evaporates from the surface, diffuses into the bulk and locally smoothes any topographical defects, such as Pt grain boundaries, as inferred from the cross-sectional EDX maps in Fig. 4. It should be noted that the annealing time becomes an important parameter. Graphene synthesis can be started shortly after the SiO2 thin film completely reacts with Pt and the surface has a uniform chemical composition. We do not rule out chemical influences to the reaction mechanism by the silicidated Pt surface in addition to simple mechanical (liquid) effects. For example, the silicide route may produce silicon carbide as an intermediate state. Precise in situ studies would be needed to confirm the correct chemical mechanism. We also suggest that such eutectic materials...
may be suitable for use as liquid-surface substrates at low synthesis temperatures, bringing all the associated benefits.

Graphene crystallinity control. Good crystallinity is an important quality factor of CVD-grown graphene, as it offers superior electronic and tensile properties, chemical resistivity and impermeability\(^1\). The ability to control the crystallinity allows us to improve the material. A systematic investigation into the effect of the thickness of the deposited silica layer on the hexagonality of graphene flakes was conducted. We used a simple analysis technique to distinguish between different levels of hexagonality of the synthesized samples. Image processing was used to obtain a threshold to convert SEM micrographs into binary images of graphene domains (Fig. 6a–d). Each solid shape was then characterized individually with a computer script such that its pixel area and perimeter were measured to obtain a value relative to a perfect hexagon as detailed in the Methods section. The results are presented in Fig. 6e. The trend matches well with the expectation: the more silica is added, the thicker the liquid silicide layer is and thus the flakes grow more independently from the underlying solid substrate. The value of the hexagonality saturates at 800-nm-thick silica layer with a 91% similarity to a perfect hexagon. Another important quality indicator, the uniformity of the shapes, also decreases significantly from about 50% fluctuation at 0 nm to less than 5% at 800 nm, as shown by the error bars. Usable silica thicknesses are limited by the thickness of the Pt foil. If there is too much silica (>2 μm) the 25 μm Pt foil can start to degrade (Fig. 4c) or curl during the synthesis due to thermal stress caused because of the differences in the thermal expansion coefficients of Pt and silica. In addition, the silicide layer may undergo a phase change during cooling resulting in the formation of striations that may induce aligned cracks in graphene (Supplementary Fig. 3). A thin silica film is thus beneficial to avoid the formation of tall striations.

Although there is as yet no confirmed theory that explains the poor crystallinity of graphene on pristine Pt via CVD that we have observed, it is well known that the face-centred cubic (FCC) lattice of Pt has the largest lattice constant compared with the commonly used transition metals for graphene synthesis. On Cu(111) the lattice constant mismatch with graphene is 3.6%, whereas on Pt(111) this is significantly higher at 12.5%. This may result in incommensurable growth and the observed poor crystallinity.

Discussion

In this study, we demonstrate a novel, low-cost substrate processing procedure to achieve rapid, efficient synthesis of millimetre-sized single crystal graphene. Silicidation of polycrystalline foils may be used as a replacement for expensive single-crystal substrates or as an alternative to polishing and grain enlargement. Large topographic defects, such as grain boundaries, are locally smoothed and the lattice of the grains is screened by a liquid surface, making silicidated polycrystalline foils superior to single crystals due to epitaxy-free synthesis. This ensures that graphene grows as a single crystal in its undistorted hexagonal shape. Silicidated polycrystalline Pt also exhibits low graphene flake nucleation density of up to 0.3 mm\(^{-2}\) and enhanced growth rates of up to 120 μm min\(^{-1}\) at elevated temperatures, allowing...
To synthesize graphene, a mixture of CH₄ (99.5%) and H₂ was introduced. The gas was annealed at 1,050°C for 5 min to improve the adhesion of graphene to SiO₂. The stack was then placed in acetone (99.99%, Sigma-Aldrich) for 6 h and after dried with a N₂ stream.

Graphene characterization. Raman spectra and maps were recorded with a Horiba LabRAM Aramis microscope equipped with a 532 nm laser. Routine SEM characterization was done with a JEOL JEM-6500F microscope at 5 kV. TEM images and SAED patterns were recorded with a JEOL JEM-2010 microscope at 200 kV, EELS measurements were performed using a CTEM (Amay Research).

Methods

Substrate preparation. Pristine Pt substrates (25 μm, Goodfellow, 99.95% purity) were used to determine the adhesion of graphene on Pt. To form a Pt/SiO₂ stack, a film of SiO₂ of specified thickness (Fig. 6b) was deposited onto pristine Pt via CVD with a tetraethyl orthosilicate (TEOS) precursor. For example, a SiO₂ film of 1 μm thickness can be deposited on pristine Pt with CVD by passing Ar gas (350 sccm) through a TEOS precursor in a ‘bubbling’ chamber that is carried to a furnace with the substrates heated to 700°C for 30 min. Other methods, such as Si, SiO₂, SiO evaporation, sputter coating, sol-gel processes or ion implantation are also applicable.

Graphene synthesis. Pristine Pt or the Pt/SiO₂ stack was placed on a boron nitride holder inside a fused silica tube (28 mm inner diameter) at sufficient distance from the walls of the tube. The tube was then purged with Ar (99.999% purity) and shifted into a pre-heated furnace, followed by annealing in H₂ (99.999%, 200 sccm) to allow Pt silicidation and to stabilize the temperature of the furnace. The useful annealing time to form silicidated Pt was strongly dependent on the temperature and the silica thickness. For example, at 1,070°C with 1-μm-thick silica layer, 30 min was suitable (typically used, also for higher temperatures). However, at 1,050°C with a 1-μm silica film after 30 min, 10% of the SiO₂ film still remained. In the experiments where reusing silicidated Pt was tested, we shortened the annealing time to 5 min to simply re-heat the solidified silicide.

To synthesize graphene, a mixture of CH₄ (99.5%) and H₂ was introduced. The gas was annealed at 1,050°C for 5 min to improve the adhesion of graphene to SiO₂. The stack was then placed in acetone (99.99%, Sigma-Aldrich) for 6 h and after dried with a N₂ stream.

Hexagonality analysis. MATLAB was used to find an automatic threshold value of SEM micrographs, which were then converted into binary images. The ratio of the perimeter (P) squared to area (A) was calculated for each geometric shape. This unit-less number is usually indicative of specific geometric shapes. For example, for a circle it is πr²/4A (the lowest possible value), for an octagon it is 16/8A, for a square it is 16 and so on. Concave polygons have P²/A values. If the calculated ratio (P²/A) for a shape is X, then we define the hexagonality as 1 – |X − 1/√192|/192 (or as a percentage, multiplied by 100%). This means that a shape with a value close to 100% is close to a perfect hexagon. The s.d. of the % hexagonality for a sample indicates how non-uniform the shape distribution is. It is understood that rounded convex or concave polygons may introduce an uncertainty in the measurement, since, for example, a rounded cube may have the ratio of the perimeter squared to area similar to a hexagon. However, we usually have either hexagonal shapes (silicidated Pt) or concave polygons (pristine Pt); thus, for a large number of graphene domains the approach characterizes the samples sufficiently.

Substrate characterization. The thickness of the SiO₂ films was measured with a Nanometrics Nanospec AFT interferometer on co-deposited Si wafers. Some samples were also analysed with ellipsometry directly on a Beaglehole Instruments Picrometer Ellipsometer. The XPS measurements were performed at base pressure of 5 × 10⁻¹⁰ torr on a VG nine channel CLAM4 electron energy analyser with a 250 W Xe X-ray excitation. XRD analysis was performed on the Bruker D800 diffractometer.

Electronic properties. Eight-leg Hall bars (15 μm × 130 μm) were fabricated using e-beam lithography followed by oxygen plasma etching. A two-step ohmic contact method was used with thermally evaporated Cu/Au outer contacts and Au-only inner contacts (Fig. 2e). The final devices were coated in ma-N 2405 photoresist as a dielectric layer and a corona discharge technique was employed to control the charge carrier density. Electrical measurements were carried out at 1.4 K in an Oxford Instruments 21 T superconducting magnet, where magnetic fields were applied perpendicular to the sample surface. A small AC field with peak amplitude of 40 μT was applied in the longitudinal direction (Bₜ). The longitudinal voltage Vₓₓ and the Hall voltage Vᵧᵧ (Fig. 2e) were simultaneously measured using the standard lock-in technique. The longitudinal resistivity ρₓₓ and the Hall resistivity ρᵧᵧ were determined as (W/L) Vₓₓ/L² and Vᵧᵧ/W, respectively, where L and W are the length and the width of the device.

References

1. Novoselov, K. S. et al. A roadmap for graphene. Nature 490, 192–200 (2012).
2. Wood, J. D., Schmucker, S. W., Lyons, A. S., Pop, E. & Lyding, J. W. Effects of polycrystalline Cu substrate on graphene growth by chemical vapor deposition. Nano Lett. 11, 4547–4554 (2011).
3. Zhao, L. et al. Influence of copper crystal surface on the CVD growth of large area monolayer graphene. Solid State Commun. 151, 509–513 (2011).
4. Gao, Y. et al. Domain structure and boundary shape of SiO₂ film grown on Cu(111) and Cu(100) films. J. Phys. Chem. Lett. 3, 219–226 (2012).
5. Murdock, A. T. et al. Controlling the orientation, edge geometry, and thickness of chemical vapor deposition graphene. ACS Nano 7, 1351–1359 (2013).
6. Wu, T. et al. Triggering the continuous growth of graphene toward millimeter-sized grains. Adv. Funct. Mater. 23, 198–203 (2013).
7. Gao, Y. B. & et al. Repeated growth and bubbling transfer of large single graphene sheet with millimeter-size single-crystal grains using platinum. Nat. Commun. 3, 699 (2012).
8. Zhou, H. et al. Chemical vapour deposition growth of large single crystalline monolayer and bilayer graphene. Nat. Commun. 4, 2096 (2013).
9. Yu, Q. et al. Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition. Nat. Mater. 10, 434–449 (2011).
10. Tapaszto, L. et al. Mapping the electronic properties of individual graphene grain boundaries. Appl. Phys. Lett. 100, 053114 (2012).
11. Geng, D. C. et al. Uniform hexagonal graphene flakes and films grown on liquid copper surface. Proc. Natl Acad. Sci. USA 109, 7992–7996 (2012).
12. Weatherup, R. S. et al. In situ characterization of alloy catalysts for low-temperature graphene growth. Nano Lett. 11, 4154–4160 (2011).
13. Dai, B. Y. et al. Rational design of a binary metal alloy for chemical vapour deposition growth of uniform single-layer graphene. Nat. Commun. 2, 522 (2011).
14. Shin, H. A. S. et al. Highly uniform growth of monolayer graphene by chemical vapor deposition on Cu-Ag alloy catalysts. Phys. Chem. Chem. Phys. 16, 3909–3914 (2014).
15. Yan, K., Fu, L., Peng, H. L. & Liu, Z. F. Designed CVD growth of graphene via atomic layer epitaxial growth of Cu-Ag alloy catalysts. Phys. Chem. Chem. Phys. 16, 3909–3914 (2014).
16. Sun, Y. J. et al. Direct growth of high-quality graphene on high-kappa dielectric SrTiO₃ substrates. J. Am. Chem. Soc. 136, 6574–6577 (2014).
17. Zhao, L. et al. Transfer-free fabrication of epitaxial graphene from its metal substrate. Nano Lett. 12, 4503–4507 (2012).
18. Vlassiouk, I. et al. Role of hydrogen in chemical vapor deposition growth of large single-crystal graphene. ACS Nano 5, 6069–6076 (2011).
19. Guselnikov, L. E. & Nametkin, N. S. 1,1-Dimethyl-1-silaethylene - heat of formation, ionization-potential and the energy of the silicon-carbon pi-bond. J. Organomet. Chem. 169, 155–164 (1979).
20. Kua, J., Faglioni, F. & Goddard, W. A. Thermochemistry for hydrocarbon intermediates chemisorbed on metal surfaces: CHn-m(CH3)m with n = 1, 2, 3 and m < n on Pt, Ir, Os, Pd, Ph, and Ru. J. Am. Chem. Soc. 122, 2309–2315 (2000).
21. Long, L. H. & Norrish, R. G. W. The thermochemistry of carbon - valence states, heats of sublimation and energies of linkage. Proc. R. Soc. London Ser-A 187, 337–357 (1946).
22. Vlassiouk, I. et al. Graphene nucleation density on copper: fundamental role of background pressure. J. Phys. Chem. C 117, 18919–18926 (2013).
23. Sun, J. et al. Growth mechanism of graphene on platinum: Surface catalysis and carbon segregation. Appl. Phys. Lett. 104 (2014).
24. Ping, J. L. & Fuhrer, M. S. Carbon impurities on graphene synthesized by chemical vapor deposition on platinum. J. Phys. Appl. 116 (2014).
25. Malard, L. M., Pimenta, M. A., Dresselhaus, G. & Dresselhaus, M. S. Raman spectroscopy in graphene. Phys. Rep. 473, 51–87 (2009).
26. Meyer, J. C. et al. On the roughness of single- and bi-layer graphene membranes. Solid State Commun. 143, 101–109 (2007).
27. Moser, J., Verdaguer, A., Jimenez, D., Barreiro, A. & Bachhold, A. The environment of graphene probed by electrostatic force microscopy. Appl. Phys. Lett. 92, 123507 (2008).
28. Lafiq, M. et al. Graphene on a hydrophobic substrate: doping reduction and hysteresis suppression under ambient conditions. Nano Lett. 10, 1149–1153 (2010).
29. Tzalenchuk, A. et al. Towards a quantum resistance standard based on epitaxial graphene. Nat. Nanotechnol. 5, 186–189 (2010).
30. Alexander-Webber, J. A. et al. Phase space for the breakdown of the Quantum Hall effect in epitaxial graphene. Phys. Rev. Lett. 111, 096601 (2013).
31. Mattei, C., Kim, H. & Chhowalla, M. A review of chemical vapour deposition of graphene on copper. J. Mater. Chem. 21, 3324–3334 (2011).
32. Gannett, W. et al. Boron nitride substrates for high mobility chemical vapor deposited graphene. Appl. Phys. Lett. 98, 242105 (2011).
33. Lamber, R. & Jaeger, N. I. On the reaction of Pt with SiO2 substrates: Observation of the Pt3Si phase with the Cu3Au superstructure. J. Appl. Phys. 70, 457–461 (1991).
34. Wang, D. et al. Silicide formation on a Pt/SiO2 model catalyst studied by TEM, EELS, and EDXS. J. Catalysis 219, 434–441 (2003).
35. Penner, S. et al. Platinum nanocrystals supported by silica, alumina and ceria: metal–support interaction due to high-temperature reduction in hydrogen. Surf. Sci. 532–535, 276–280 (2003).
36. Gannett, W., Lamber, R. & Jaeger, N. I. Dielectric degradation of Pt/SiO2/Si structures during thermal annealing. Solid-State Electronics 36, 583–593 (1993).
37. Grunthaner, P. J., Grunthaner, F. J. & Madhukar, A. Chemical bonding and charge redistribution - valence band and core level correlations for the Ni/Si, Pd/Si, and Pt/Si systems. J. Vac. Sci. Technol. 20, 680–683 (1982).
38. Nguyen, T. P. & Lefranc, S. XPS study of SiO thin-films and SiO metal interfaces. J. Phys. Condens. Mater. 1, 5197–5204 (1989).
39. Chou, T. C. Anomalous solid-state reaction between SiC and Pt. J. Mater. Res. 5, 601–608 (1990).
40. Xu, L. L., Wang, J., Liu, H. S. & Jin, Z. P. Thermodynamic assessment of the Pt-Si binary system. Calphad 32, 101–105 (2008).
41. Huang, P. Y. et al. Grains and grain boundaries in single-layer graphene atomic patchwork quilts. Nature 469, 389–392 (2011).
42. Baker, A. M. R., Alexander-Webber, J. A., Altebarumer, T. & Nicholas, R. J. Energy relaxation for hot Dirac fermions in graphene and breakdown of the quantum Hall effect. Phys. Rev. B 85, 115403 (2012).
43. Larson, A. et al. Tuning carrier density across Dirac point in epitaxial graphene on SiC by corona discharge. Appl. Phys. Lett. 105, 063106 (2014).

Acknowledgements
The work at Oxford University Materials Department is supported by the DTA-EPSRC (V.B., J.B.), the Commonwealth Scholarship Commission (A.T.M.), University of Oxford Clarendon Fund (A.T.M.), the Royal Society (N.G.), the European Research Council (ERC-2009-StG-240580) (N.G.), the Engineering and Physical Sciences Research Council (N.G.). The work at Oxford University Physics Department is supported by the EPSRC.

Author contributions
N.G., V.B. conceived and designed the investigation. V.B. carried out the CVD synthesis and optimization, transfer experiments, TEM characterization, data analysis and wrote the manuscript. V.B., A.T.M., A.K., J.B., performed SEM characterization. V.B., A.K. performed Raman characterization. N.G. oversaw project direction, planning and infrastructure. A.C. carried out the XPS measurements. P.H. carried out the XRD measurements. J.M. performed the AFM measurements. J.A.A.-W., J.H. and R.J.N. carried out the Quantum Hall device fabrication, measurements and data analysis. All authors discussed the results and commented on the manuscript.

Additional information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

How to cite this article: Babenkov, V. et al. Rapid epitaxy-free graphene synthesis on silicidated polycrystalline platinum. Nat. Commun. 6:7536 doi: 10.1038/ncomms8536 (2015).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/