Graphene film growth on polycrystalline metals

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CONSPECTUS

Graphene is a true wonder material and is the newest member of the nanocarbon family. The continuous network of hexagonally arranged carbon atoms give rise to some exceptional electronic, mechanical and thermal properties, which could see the application of graphene in new generation electronic components, energy-storage materials such as capacitors and batteries, polymer nanocomposites, transparent conducting electrodes and mechanical resonators. The application that has caught the eye of many is that of optically transparent conducting electrodes or films where graphene has the potential to rival indium tin oxide (ITO) and be used in next generation displays, solar cells and sensors. Typically, graphene has been produced from graphite using a variety of methods however these techniques are not suitable for growing large-area graphene films. Much effort has therefore been focused on developing methodology to grow graphene films across extended surfaces. Graphene film growth can be achieved on a variety of polycrystalline metal substrates using a range of experimental conditions. In particular graphene films can be grown over Group 8 metals, iron and ruthenium; Group 9 metals, cobalt, rhodium and iridium; Group 10 metals, nickel and platinum; Group 11 metals, copper, gold. It has also

proved possible to grow graphene films over alloys such as stainless steel and other commercial copper-nickel alloys. At present copper and nickel dominate the field, producing large-area films that have already been efficiently transferred and tested in a number of electronic devices. Graphene has even been grown over 30 inches in width on copper and subsequently transferred onto a display plastic ready for incorporation into new generation displays. Looking to the future high quality, reproducible growth at ambient pressure and low temperature from cheap, readily available carbon sources will be important for the further development of graphene films in commercial applications. The growth of graphene on metal surfaces does have its drawbacks in that it is necessary to transfer the graphene from the metal or to remove the metal by etching. Thus there is still much to do in the field.

1.0 Introduction

Graphene is a single layer of graphite and is the newest member of the nanocarbon family. The continuous network of hexagonally arranged carbon atoms give rise to some exceptional electronic, mechanical and thermal properties, which could see the application of graphene in new generation electronic components, energy-storage materials such as capacitors and batteries, polymer nanocomposites, transparent conducting electrodes and mechanical resonators.[1-3] Graphene can be prepared using ‘top-down’ approaches from graphite such as micromechanical cleavage, oxidation and thermal expansion followed by reduction, and by extensive sonication in solvent systems with surface energies that match that of graphite.[1,4] ‘Bottom-up’ methods of graphene synthesis, that are perhaps more amenable to scale, have included decomposition of ethanol in a microwave plasma[5] and the spray pyrolysis of sodium ethoxide.[6] It is also possible to obtain graphene by the longitudinal cutting of carbon nanotubes.[7] All of these methods produce platelets of graphene. However, this account will focus on the synthesis, mainly by chemical vapour deposition (CVD) and temperature-programmed growth (TPG), of large area graphene films. This is a highly relevant topic given the excitement around producing optically transparent conducting films that could rival indium tin oxide (ITO) and be used in next generation displays, solar cells and sensors or that could even be patterned to make new electronic components and devices. It is worth mentioning that graphene films can be grown on silicon carbide wafers by high temperature reduction and represents a very active area of research in electronic devices, that has been reviewed recently, and will not be discussed here.[8] This account details current progress in the formation and control of graphene films on polycrystalline metal surfaces.

1.1 Introduction to growth on metal surfaces

There are a number of factors that affect the potential of a metal to produce high quality graphene films; from an industrial point of view cost is important as metals are normally etched during the transfer process, but more fundamental differences between the metals also play a big part in their selection. Metals can promote graphene formation by a surface growth mechanism, where the metal catalyses the decomposition of a carbon feedstock promoting carbon fragmentation at the metal surface, or by segregation where carbon is absorbed in the metal at high temperature and then segregates to the surface forming graphene on cooling. Many of the inferences about graphene growth on metals have been made based on information gained from density function theory (DTF) calculations and experimental observations from single-crystal systems.[9] While these studies provide valuable insight into the effect of interaction strength and lattice mismatch on graphene growth along with the mechanism of formation, single crystal systems are not suitable for the production of large-scale graphene film. This is primarily due to the difficulty in growing large single-crystal metals. Instead the future of large-scale graphene film production lies with polycrystalline metal films, which can be deposited on substrates of variable size using techniques such as sputtering or evaporation.

In order for applications to develop it is important that graphene films formed on metal surfaces can be removed or transferred to other substrates, in particular plastics on which it is difficult to grow graphene directly. Typical methods of film transfer have included stamping using poly(methyl methacrylate) (PMMA) or polydimethylsiloxane (PDMS),[10,11] where the polymer is added to the graphene surface, the metal removed via chemical etching, the graphene/polymer stamped onto a second substrate and the polymer removed. It is also possible to use rolling or ‘roll-to-roll’ processes that are compatible with industry techniques, where graphene grown on flexible metal films is rolled onto flexible substrates, followed by removal of the metal layer to yield bare graphene on the substrate surface.[12] The transfer of 30 inch graphene films grown on Cu has been achieved using the roll-to-roll process.[13]

2.0 Large-area growth of graphene on polycrystalline metal surfaces

The growth of large-area graphene films requires large metal surfaces, which are generally prepared by sputter coating or electron beam evaporation of the desired metal. This results in metal films with multiple grains that are then typically annealed to improve surface roughness and/or to promote formation of a particular metal facet. Selecting metals suitable for large-scale graphene growth is complicated by a number of additional considerations that are not relevant for growth on single crystals. Key to this is the behaviour of graphene towards grain boundaries in the underlying metal. Growth over grain boundaries or large metal grain sizes is favourable for high quality graphene as underlying grain boundaries often result in graphene defects including nucleation of multilayer graphene.[14] Grain size is ultimately related to the metal film thickness,[15] with larger grains forming for thicker films, however as metal thickness is also a key factor for graphene growth over certain metals,[16] enlarging grain size by using thicker metal films is not appropriate in all cases. Larger grains can be promoted by annealing at high temperatures but surface defects such as pits can be formed during this process that can degrade the quality of the graphene.[16,17]

A study on engineering polycrystalline Ni films to achieve improved uniformity of CVD grown graphene highlights a number of additional factors that affect metal grain size, including the temperature and pressure conditions during the initial metal deposition, and the method used to prepare the underlying SiO_2/Si substrate.[17] Furthermore improved graphene uniformity for metal films deposited on c-plane sapphire rather than SiO_2/Si has been reported for multiple metals due to preferred single crystal metal growth over sapphire.[18-21] It is also important to reduce the number of graphene nucleation sites as defects can form at graphene domain boundaries due to misalignment of the carbon atoms.[22] For surface catalysed reactions the number of graphene nucleation sites can be controlled not only by the reduction of surface defects of the metal, but also by the rate of carbon exposure, where slower rates result in fewer nucleation sites and hence larger graphene domains.[23] This prolonged exposure to the growth temperature to reduce graphene nucleation must be balanced with the detrimental effect that prolonged exposure may have on the metal surface and the graphene quality.

Graphene growth on single crystals should provide some insight into the expected growth of graphene on polycrystalline surfaces with regard to the number of layers anticipated. However, care must be taken as many of the single crystal studies are performed under ultra-high vacuum (UHV) conditions, whereas atmospheric pressure conditions are generally more favourable for growth at the industrial scale due to cost of maintaining low pressure systems. Graphene growth has been seen to alter with pressure, for example while growth on Cu has been found to be 'self-limiting' to monolayer graphene at UHV, few layer graphene has been observed for atmospheric pressure growth.[24]

2.1 Group 8

2.1.1 Iron

Studies on polycrystalline Fe generally report the growth of multilayer graphene via CVD at low pressures and relatively low temperatures (600 – 800 °C). The exposure to acetylene is found to be important to graphene formation, with both reduced surface coverage and reduced graphene thickness being observed at lower exposures.[25] Graphene thickness can also be controlled using Fe film thickness,[26] with thinner graphene forming on thicker Fe. Interestingly for Fe films 6 – 20 nm thick multilayer graphene grew on-top of carbon nanotubes (CNTs) while for films <5 nm CNTs were formed exclusively. Increasing growth temperature is found to increase graphene thickness but reduce the number of defects,[25] so growth of thin, high quality graphene on Fe requires careful balancing of conditions.

2.1.2 Ruthenium

Growth of graphene on Ru sputtered coated on SiO_2,[27] fused silica and sapphire has been reported.[18,28] The Ru films deposited on SiO_2 and fused silica have a columnar structure with strongly aligned grains exposing flat (0001) surface facets, whereas on sapphire the Ru is described as being 'single crystalline' Ru(0001). Exposure to ethylene at high temperatures (800 °C,[28] 950 °C[18,27]) followed by slow cooling in UHV affords uniform monolayer graphene that is continuous across grain boundaries and is ‘slightly wavy’ in appearance.[27] Etching of the underlying Ru deposited on sapphire, using an aqueous solution of ceric ammonium nitrate and acetic acid, has been demonstrated for monolayer graphene with domains <60 μm in size,[18] where the growth is halted prior to formation of the continuous graphene film. The etchant is said to etch down between the graphene domains then sideways underneath them to release the graphene so may not be suitable for continuous films where access to the underlying Ru would be restricted.

2.2 Group 9

2.2.1 Cobalt

A number of studies have been undertaken for the growth of graphene on polycrystalline Co deposited on SiO_2/Si,[16,29,30] along with growth over c-plane sapphire.[19] CVD of methane at high temperature affords a uniform monolayer of graphene for Co deposited over sapphire (single crystalline Co) but an inhomogeneous film containing both monolayer and multilayer graphene flakes for Co deposited over SiO_2/Si (polycrystalline Co, grain size <3 μm). This is attributed to the high density of Co grain boundaries in the SiO_2/Si based sample, Figure 1.

<Figure 1>

Non-uniform graphene of varying thickness has been reported for CVD of acetylene over Co at low pressures and moderate/high temperatures (800 – 1000 °C). Graphene thickness is seen to decrease with shorter growth times and increased temperature, which can be attributed to reduced carbon exposure and the increased desorption coefficient of carbon at higher temperatures.[29] Co film thickness is also found to be an important factor as the percentage of multilayer graphene decreases with decreasing Co thickness,[16] resulting in 80% monolayer graphene for 100 nm Co films. Thinner Co films (~60 nm) agglomerated and formed surface pits so entirely monolayer growth could not be achieved. Multi-layer graphene is seen to nucleate at grain boundaries,[30] and growth of uniform, monolayer graphene has been reported for single crystalline Co deposited over sapphire.[19] Etching of Co to release graphene has been demonstrated using aqueous solutions of $FeCl_3$ and HCl.[19,29]

2.2.2 Rhodium

Graphene formation on Rh foils, repeatedly annealed under UHV to promote the emergence of the Rh(111) face, have been reported.[31] Growth via carbon segregation occurs after exposure of the metal surface to benzene vapour, where graphene islands begin to form upon reaching the carbon solubility limit of Rh. These islands coalesce resulting in complete surface coverage of monolayer graphene. However, multi-layer graphene forms upon cooling due to further segregation of carbon from the bulk metal, highlighting the importance of growth temperature for the control of graphene thickness.

2.2.3 Iridium

Graphene growth has been reported on single crystalline Ir(111) films deposited on sapphire and yttria stabilised zirconium oxide (YSZ) by pulsed laser deposition and electron beam evaporation respectively.[20,32] On sapphire, high quality monolayer graphene was grown via CVD of ethylene at 677 °C under UHV conditions, and found to cover >95 % of the surface for 10 min carbon exposure. Whereas, for YSZ, temperature programmed growth (TPG) of Ir(111) exposed to acetone (the carbon source) graphene formation begins around 327 °C and proceeds to a well ordered graphene monolayer upon heating to 727 °C.

2.3 Group 10

2.3.1 Nickel

CVD growth of graphene over polycrystalline Ni has primarily been performed at atmospheric pressure, yielding graphene that extends across nickel grain boundaries to form continuous films.[33,34] Slow annealing of the polycrystalline nickel,[35] or increase in deposition temperature,[17] promotes large grain sizes of Ni(111) over Ni(100) improving graphene film quality. A study on the effect of growth temperature, gas mixing ratio and growth time on the CVD of acetylene/hydrogen shows that high temperature, high hydrogen concentration and short growth time are important for producing few-layer graphene with minimal defects.[36] A similar study involving methane showed the importance of cooling rate and short growth times for reducing graphene thickness to grow primarily single and bilayer graphene films.[14,37] Etching of nickel to release graphene has been widely demonstrated using aqueous $FeCl_3$,[37] enabling the study of nickel-grown graphene in a number of electronic devices.[38]

Growth of graphene on nickel surfaces has also been demonstrated based on diffusion and segregation of carbon from underlying amorphous carbon or nanodiamond films.[39,40] Conversely nickel films have been shown to transform the underlying carbon source to graphene at high temperature, forming bilayer graphene films directly on insulating substrates from polymers or self-assembled monolayers (SAMs) at low pressure conditions,[41] and few-layer graphene on SiO_2/Si from SAMs at atmospheric pressure, Figure 2.[42]

<Figure 2>

2.3.2 Platinum

The growth of uniform monolayer and bilayer graphene films has been achieved for CVD of methane at low pressures and high temperatures (1000 – 1050 °C). Temperature is found to be an important factor for controlling graphene thickness, with thicker films (>5 layers) being produced at higher temperatures.[43] Graphene uniformity is seen to alter with carbon exposure, forming irregularly shaped islands of bilayer graphene upon increasing growth time or flow rate of carbon sources, Figure 3.[44]

<Figure 3>

2.4 Group 11

2.4.1 Copper

Graphene growth on Cu foils has been extensively studied under both low and ambient pressure conditions, and has been reviewed recently.[45] An early study reported the growth of centimetre scale graphene films on Cu foils via high temperature CVD of methane under UHV conditions.[46] These films were characterised as ~95 % monolayer with small regions of bi- and multi-layer graphene and were found to be ‘self-limiting’; producing similar films for short and long methane exposures. Graphene thickness is found to be independent of copper thickness, with similar graphene films being observed for foils of thickness between 12.5 – 50 mm. A similar method has been utilised for the production of >95 % monolayer films on Cu foils with a diagonal length up to 30 inches.[13] Here curving of the Cu foils around a 7.5 inch quartz tube is necessary to combat graphene inhomogeneity brought about due to the temperature gradient across the radius of the tubular reactor. For both of these studies higher quality graphene is observed for larger grain sizes. The effect of Cu purity and pre-treatment on UHV graphene growth have been investigated along with the effect of hydrocarbon concentration.[47] Sonication in acetone prior to annealing and the reduction of annealing pressure from 80 to 20 mbar were found to be beneficial to graphene uniformity, while Cu purity was found to impact graphene thickness, with monolayer graphene reported on 99.999 % Cu foil and bilayer graphene being reported for 99.8 %. Hydrocarbon concentration can also impact graphene uniformity due to its effect on the number of graphene nucleation sites; with few sites, and hence more uniform graphene, being produced at lower hydrocarbon concentrations. Growth of graphene with average domain sizes of ~140 μm^2 has been reported for a low pressure CVD using carefully controlled hydrocarbon exposures.[23] Methane exposure is kept low at the beginning of the process, to reduce the number of graphene nucleation sites, and then increased during the reaction to promote continuous graphene coverage, Figure 4.

<Figure 4>

Under ambient pressure conditions, graphene growth on large polycrystalline Cu films using methane as the carbon source occurs readily,[48,49] and is continuous across Cu grain boundaries.[50] Using these conditions predominately mono- and bi-layer graphene is formed when using Cu (700 nm) deposited on SiO_2/Si.[48] When using electropolished Cu foils, 95 % monolayer coverage can be obtained under low methane concentrations, whilst increasing the methane concentration affords thicker graphitic regions.[49] Similarly, chemical mechanical polishing of Cu foils results in improved graphene films when compared to unpolished samples. This can be attributed to the reduction in graphene nucleation sites on the smoother metal surfaces.[51]

An alternative method of graphene growth on Cu foils involves depositing the carbon source on the metal surface prior to heating to high temperatures. Using this method, growth of monolayer graphene has been achieved by annealing Cu foils with an amorphous carbon coating at 1035 °C under a flow of hydrogen.[52] The flow of hydrogen was also found to be important for growth of graphene at 800 °C on Cu foils coated with PMMA, where graphene thickness was controlled by adjusting argon and hydrogen flow rates, forming monolayer graphene at higher hydrogen flows.[53] Monolayer growth for Cu covered with sucrose and fluorine has also been reported under the same conditions. The growth of monolayer graphene can even be achieved by heating ‘food’, ‘insects’ or ‘waste’ deposited on Cu to 1050 °C.[54] Etching of copper has been reported using aqueous solutions of iron chloride,[49] ammonium salts,[47] or by using Cu etchant solution (CE-100, Transene).[51]

2.4.2 Gold

Ambient pressure CVD growth of graphene on gold has been reported for gold foils 25 μm thick.[55] The partially (111) orientated gold surfaces exposed to methane at 850 - 1050 °C produce a high percentage of monolayer graphene. Temperature has a minimal effect on graphene thickness and defect concentration for this range, but higher temperatures resulted in the formation of highly defective multilayer graphene. Etching of the gold to allow film transfer is readily achieved using the commercial gold etchant TFA from Transene Co. Inc., which contains a $KI-I_2$ complex.

2.5 Alloys

2.5.1 Stainless steel

Inhomogeneous growth of graphene films has been reported by CVD at moderate temperature (800 – 850 °C) in both low and ambient pressure conditions. The rate of cooling is found to be an important factor, with no graphene being detected for high cooling rates ≥140 °C/min and graphite-like material being formed for very slow cooling rates.[56] Interestingly, the duration of carbon exposure has a less marked influence on mono, bi or multi-layer graphene formation, although it is noted that longer exposure times resulted in higher quality graphene and significantly shorter exposure times resulted in discontinuous graphene growth.[57]

2.5.2 Copper – Nickel alloy

Cu-Ni alloys can be used for graphene growth where the substrates are initially prepared as Cu/Ni/SiO_2/Si sandwich structures,[58,59] and the Cu-Ni alloy formed in situ upon high temperature annealing under UHV, Figure 5. Carbon impurities in the nickel film (~2.6 atom %) act as the carbon source, diffusing along with the Ni atoms during the high temperature annealing, resulting in graphene formation on the surfaces of the Cu-Ni binary alloys. The number of graphene layers synthesised varied depending on the thickness of the Ni layer deposited; for 20 nm Ni (5.5 atom % Ni) ~95 % of the surface was covered with monolayer graphene, and for 40 nm Ni (10.4 atom % Ni) ~90 % of the surface was covered with bilayer graphene. At higher atom %, of Ni graphene growth becomes inhomogeneous, forming randomly distributed regions of multilayer graphene. Graphene growth also occurs on commercial, polycrystalline Cu-Ni alloy films 200 nm thick (67.8 weight % Cu and 31 weight % Ni) using methane as the carbon source,[60,61]

<Figure 5>

2.5.3 Gold – nickel alloy

Au-Ni alloys prepared by from Au films (0 – 10 nm) thermally evaporated onto polycrystalline Ni films (~550 nm) on SiO_2/Si substrates can be used to grow graphene with acetylene as the carbon source.[62] Graphene films with ~74 % monolayer coverage and domain sizes >15 μm is achieved for growth over the Ni-Au (5 nm Au) based alloy at 450 °C under low pressure conditions. Pre-annealing at 600 °C (under hydrogen) is vital for graphene formation. Successful etching away of the alloy can be achieved using a two-step process involving aqueous solutions of $FeCl_3$ and KI/I_2.

2.5.4 Nickel – molybdenum alloy

Growth of entirely monolayer graphene with 100 % surface coverage can be achieved from CVD of methane at 1000 °C over a Ni-Mo alloy.[63] The alloy was prepared by deposition on Ni (200 nm) onto Mo foils (25 or 200 μm) and annealed at 900 °C prior to graphene growth. Graphene formation proceeds via a surface catalysed process rather than from carbon segregation as carbon dissolved in the bulk is ‘trapped’ as molybdenum carbide.

3.0 Summary

Graphene film growth on a variety of polycrystalline metals and metal alloys has been demonstrated across a range of experimental conditions, providing insight into the key factors effecting growth and the potential of different metals to produce high quality graphene. At present Cu and Ni dominate the field, producing large area films that have already been efficiently transferred and tested in a number of electronic devices. Looking to the future high quality, reproducible growth at ambient pressure and low temperature from cheap, readily available carbon sources will be important for the realisation of graphene films in commercial applications. A further, important advancement will be high quality graphene growth directly on insulating substrates, which is an area of growing interest in the field.

FIGURES

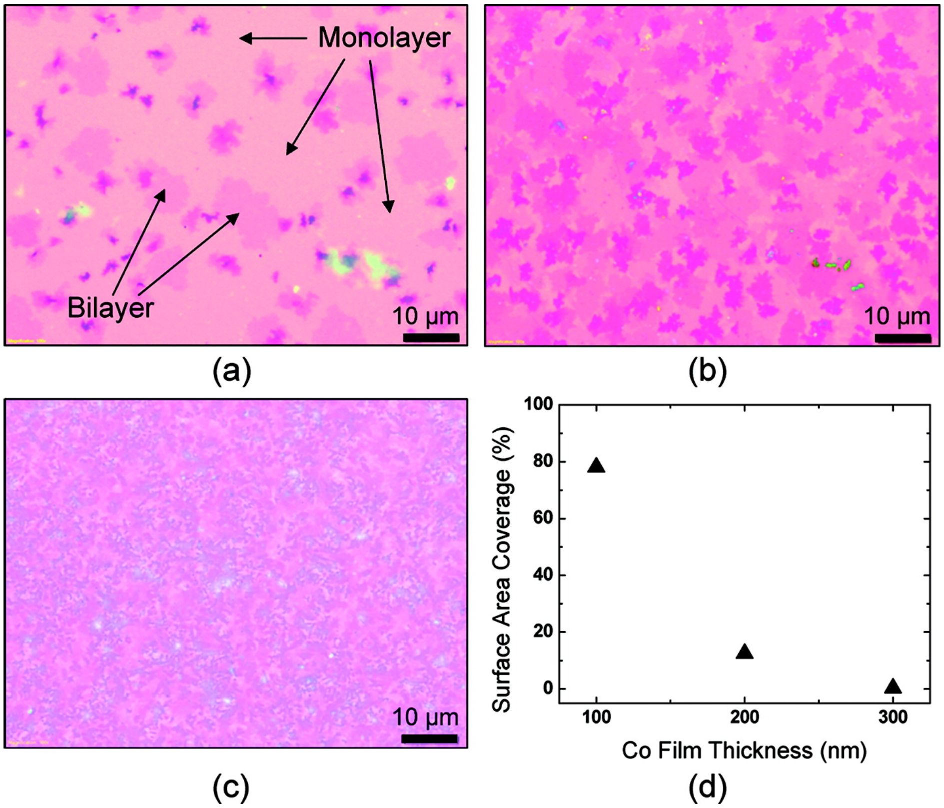

Figure 1. Optical micrographs of graphene grown on (a) 100 nm Co film, showing large monolayer area along with small domains of bi- and multilayer area, and (b) 200 nm and (c) 300 nm Co films. (d) Percentage surface area coverage by monolayer graphene as a function of Co film thickness. [16]

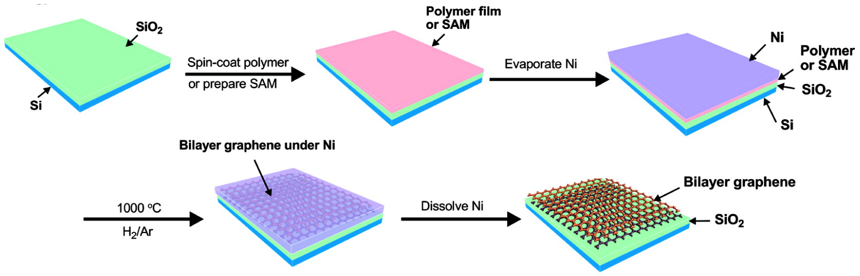

Figure 2. Schematic of bilayer graphene formation from Ni coated polymers or SAMs on SiO_2/Si substrates after annealing at high temperature under hydrogen.[41]

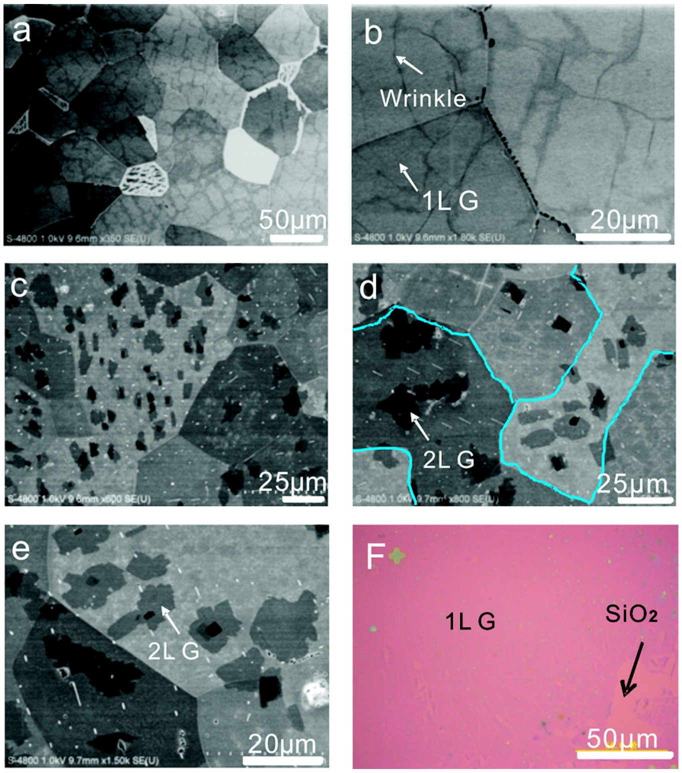

Figure 3. SEM image of single-layer graphene grown on Pt foils (a,b). SEM images (c–e) show sequential growth of bilayer flakes with orthogonal and irregular boundaries on Pt domains (brighter SEM contrast). (f) Optical image of monolayer graphene transferred onto a 300 nm SiO_2/Si susbtrate.[44]

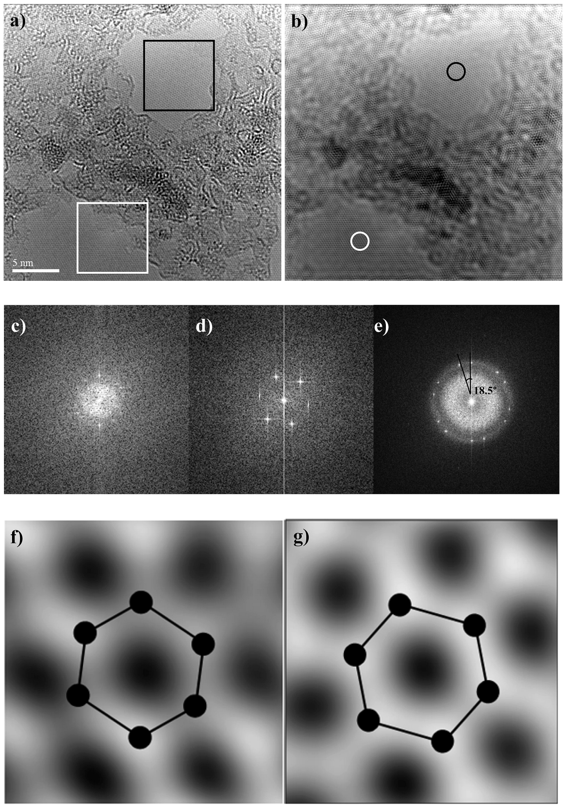

Figure 4. (a) TEM bright field image of monolayer graphene grown on Cu at a domain boundary (b) Mask-filtered image of (a). (c,d) Fast Fourier transform (FFT) from area in white and black box respectively in (a), which show that the monolayer graphene has two different crystal orientations at each respective area. (e) FFT of the whole image in (a) shows two sets of hexagonal FFT spots misoriented by approximately 18.5° from one another. (f,g) High-resolution image cropped from white and black circled regions in (b) respectively.[23]

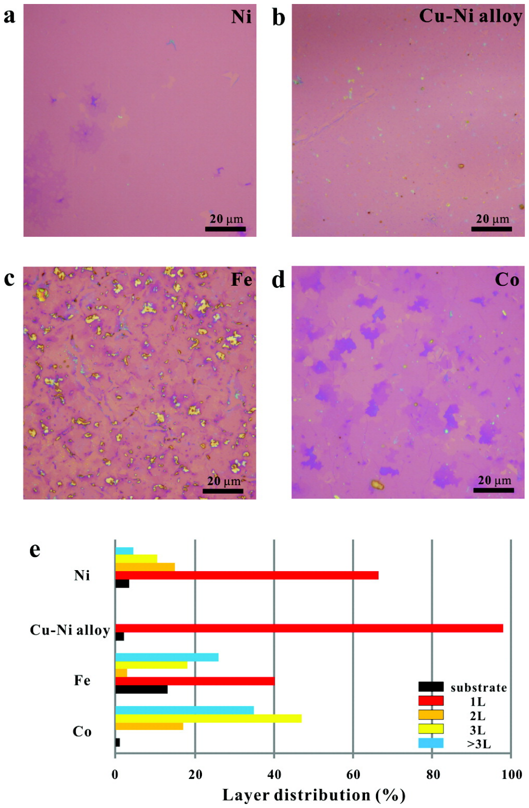

Figure 5. CVD growth and segregation behavior of graphene on Ni (a), Cu–Ni alloy (b) (5.5 at % Ni), Fe (c), and Co (d) and the corresponding layer thickness distributions at optimized growth temperature 1100, 900, 1000, and 1000 °C, respectively (e). The graphene was transferred to 300 nm SiO_2/Si substrates for taking the optical microscope images.[58]

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Rebecca Edwards received her MChem from Durham University in 2010. She is currently studying for a PhD in chemistry, researching the synthesis and chemistry of graphene, in the nanocarbon group at Durham University led by Karl Coleman.

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Conspectus Figure