**Research Article**

**Open Access**

Bing Li, Genhua Pan, Shakil A. Awan, and Neil Avent

# Techniques for Production of Large Area Graphene for Electronic and Sensor Device Applications

**Abstract:** Here we review commonly used techniques for the production of large area and high quality graphene to meet the requirements of industrial applications, including epitaxial growth on SiC, chemical vapour deposition (CVD) on transition metals and growth from solid carbon source. The review makes a comparison of the growth mechanisms, quality (such as mobility and homogeneity) and properties of the resultant graphene, limitations and the prospect of each production method. A particular focus of the review is on direct (transfer free) growth on dielectric substrate as this is potentially one of the promising techniques for graphene production which can readily be integrated into existing semiconductor fabrication processes.

## 1 Introduction

Graphene, a single-atom-thick allotrope of carbon having $sp^2$-bonded atoms in a 2-dimensional honeycomb lattice, can be regarded as a basic building block of 3D graphite, 1D carbon nanotubes and 0D fullerenes [1–3]. Graphene was first produced by the Manchester group in 2004 [1, 2], on a Si wafer with carefully chosen thickness of $SiO_2$, by the so called scotch-tape method or mechanical exfoliation. A 300 nm thick $SiO_2$ layer on the Si substrate electrically isolates the graphene and weakly interacts with it,

providing visually identifiable and nearly charge-neutral graphene layers, which make it possible to characterize the physical properties of graphene. Although graphene has been theoretically studied for over 60 years [2] and efforts to make thin films of graphite by mechanical exfoliation date back to 1990 [4, 5], only graphite films no thinner than 50 to 100 layers were produced before 2004. The significance of Manchester's results lies in the discovery of the unique electronic properties in the naturally-occurring two-dimensional material due to the unique transport properties of massless Dirac fermions. This has led to a surge of research interest in this material. More extraordinary properties of graphene have since been unearthed, such as electron mobility of $10^6 cm^2 \cdot V^{-1} \cdot s^{-1}$ at room temperature [6] (a limit up to 40000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ on $SiO_2$ substrate [7]), ultralow resistivity [2], anomalous quantum hall effect [8], different electronic transport performance in armchair or zig-zag edge orientations [9], behaviour of massless Dirac fermions [10, 11], unusual band structure [12, 13], high thermal stability [14], ultrahigh breaking strength of 1 TPa and tensile strength of 125 GPa [15], high transparency at certain wavelengths [16, 17], high chemical resistance [18], long spin diffusion length at room temperature [19], controllable doping level [20], etc. These extensive and unique properties of graphene have made the material to be known as the "21st century wonder material". It is promising for the post Moore's era [2, 12, 21], with potential technological applications in many areas including electronics [22], photonics [23, 24], biological and chemical sensors [25, 26], energy storage [27], spintronics [28–30] and quantum computing [31].

However, to realise its full potential for industrial scale applications, large scale production of high quality graphene on device compatible substrates is one of the key requirements. Significant progress in this respect has already been made since the discovery of graphene [1]. This paper aims to provide an up to date review of the production techniques for large area graphene films.

The techniques of large area graphene production developed so far can be mainly categorized into the following types [32]: epitaxial growth on SiC substrate, chemical vapour deposition (CVD) on transition metal, physical

**Bing Li, Genhua Pan:** Wolfson Nanomaterials and Devices Laboratory, School of Computing and Mathematics, Faculty of Science and Environment, Plymouth University, Plymouth, Devon, PL4 8AA, UK and Centre for Research in Translational Biomedicine, Plymouth University, Plymouth, Devon, PL4 8AA, UK
**Neil Avent:** Centre for Research in Translational Biomedicine, Plymouth University, Plymouth, Devon, PL4 8AA, UK
**Shakil A. Awan:** Wolfson Nanomaterials and Devices Laboratory, School of Computing and Mathematics, Faculty of Science and Environment, Plymouth University, Plymouth, Devon, PL4 8AA, UK and Cambridge Graphene Centre, Department of Engineering, University of Cambridge, CB3 0FA, UK

vapour deposition (PVD) with a solid carbon source. These techniques share common basic principles, which are the decomposition of inorganic or organic molecules at elevated temperatures and the formation of $sp^2$- hybridized C-C bond on catalytic surfaces. However, each method uses specific substrate and growth conditions, such as carbon source, reaction temperature, pressure, heating and cooling rates, reaction duration, types and sizes of catalytic surfaces, which may lead to different requirement of post-processing for application purposes. Here, we discuss the characteristics of each method together with their advantages and disadvantages for device applications.

# 2 Epitaxial growth from single crystal SiC substrates

Berger and his co-workers reported in 2004 [21], the same year as the discovery of exfoliated graphene [1], the epitaxial growth of ultrathin graphite films by thermal decomposition of 6H-SiC(0001) single crystals in an ultrahigh vacuum (UHV), which was perhaps the first technique reported for large area graphene production, although the solid-state graphitization mechanisms of silicon carbide had been studied well before 2004 [33, 34]. The production of monolayer epitaxial graphene was subsequently reported by the same group in 2006 [12]. When a single crystal SiC substrate is heated up to a temperature in excess of 1200 °C in an UHV chamber, the Si atoms on the surface are sublimated due to the lower vapor pressure [34–36], leaving behind C atoms on the SiC crystal surface. Because of the very small mismatch of the SiC(0001) crystal and the graphene honeycomb lattices, the carbon atoms are able to reconstruct into a graphene sheet on top of the SiC (0001) crystal surface [21, 37].

The epitaxial growth of graphene on single crystal SiC is not self-limiting. The number of layers, quality and properties of the graphene depends on whether the graphene grows on the Si or C terminated face, and also on the annealing temperatures [38, 39] and the vacuum conditions [40]. On the C terminated face, graphene tends to grow into more layers, usually more than 10 layers. The first few layers are highly electron-doped with random orientation while the subsequent layers are not as much doped as the first few layers [41]. The electronic properties of the graphene layers are affected by these electronic charges and show a mobility of $10^4$-$10^5 cm^2 V^{-1} s^{-1}$ with the corresponding carrier density of $10^{13} cm^{-2}$. In contrast, growth of graphene on the Si face is more controllable, resulting in fewer layers with improved properties [41].

However, compared with graphene grown on C terminated face, a lower mobility ($10^2$-$10^3 cm^2 V^{-1} s^{-1}$) and carrier density ($10^{13} cm^{-2}$) can be seen as the absence of electron-doped interface [42].

The major attraction of this method is the direct growth of graphene on insulating SiC wafers, therefore transfer of graphene to another insulating substrate is not required for device applications. This has provided a unique platform for exploring electronic devices, such as field effect transistors and integrated electronic circuits, which has attracted major interest in the field [43]. For example, graphene transistors operating at 100 GHz frequencies [44] and graphene integrated circuits operating at frequencies up to 10 GHz [45] have recently been developed by IBM.

However, the epitaxial technique has several limitations in meeting the industrial requirements for electronic applications. In particular, the graphene grown on the single crystal SiC wafers is not atomically flat as those on Si wafers, but with a terraced morphology [12], as typically shown in Fig. 1 [40]. The high cost of the SiC crystal starting material also renders it impractical for large-scale commercial applications. The very high growth temperature in ultra-high vacuum is another limitation.

# 3 Chemical Vapour Deposition

One of the major breakthroughs in the production of large area graphene, following the epitaxial method, is the growth of graphene by CVD method [46–48] using short chain hydrocarbon gases, such as methane and ethylene [49–53], on a catalytic surface of transition metals, such as Ni [17, 54, 55], Ru [56–58], Ir [59], Au [60], Cu [46], Pt [61], Rh [62, 63], Pd [64, 65] and Fe [66]. Short chain hydrocarbon gases have long been used in carbon nanotube growth [67, 68]. A limited number of early attempts before 2004 can also be found on the growth of very thin graphite layers or even monolayer graphite by CVD, for example, on Pt(111) by Land et al. [69], and on TiC(111) by Nagashima et al. [70], however, no attempts have been made in the characterization of the electron transport properties of these films.

In the CVD growth process, a polycrystalline metal sheet [71, 72], or metal film deposited on a substrate [73, 74], acting as a catalytic surface, is usually pre-annealed (800-1000°C) in vacuum to obtain larger crystalline grains. Short chain hydrocarbon molecules are then introduced to the chamber, where they are adsorbed on the metal surface, decompose into carbon atoms and form graphene
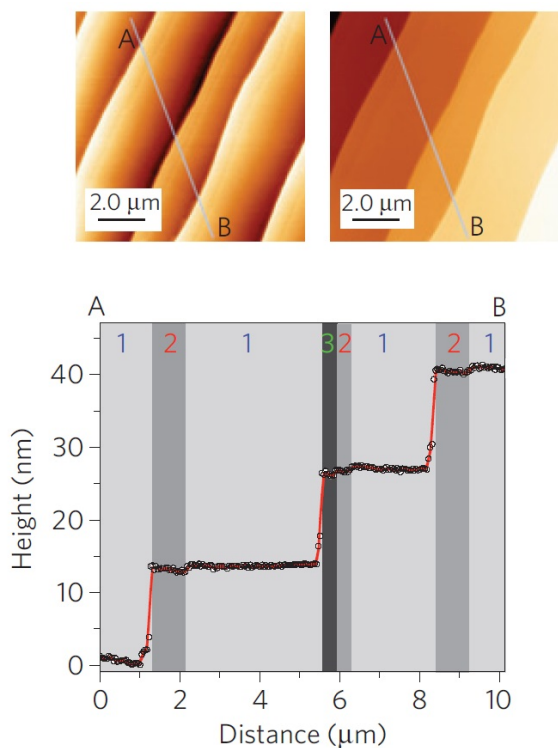
**Figure 1:** Typical terrace morphology of epitaxial graphene on single crystal SiC wafers and the terrace step height measured by AFM. Top-left: a typical AFM image from graphene formed on 6H–SiC(0001) substrate. Top-right: an AFM image of the terraces adjusted at the same height. Bottom: line profile showing height of terraces with small depressions of around 0.5 nm and 1 nm located at the very edge of the macro-step, indicating that the nucleation of new graphene layers starts at step edges of the substrate surface. Monolayer, bilayer and trilayer graphene are readily identified by the presence of 1, 2 or 3 deflection minima. Courtesy of Emtsev et al. [40].

on the metal surface. There have been different theories proposed to explain the growth mechanisms of graphene on metal surfaces. The earlier theory is based on epitaxial growth of graphic structures on hexagonal or other crystallographic surfaces, such as Co(0001) [75], Ni(111) [76], Pt(111) [75], Ru(111) [77], Ir(111) [78]. However, many of the recent experiments on the growth of graphene on variety of polycrystalline transition metals appears to support the surface catalytic effect [48] although details about the catalytic mechanism remain unclear. The recent understanding of the CVD graphene growth process is linked to the carbon solubility of the transition metals used. For metals with relatively higher carbon solubility at high temperatures, with Ni being a typical representation material [17, 54, 55], the carbon atoms dissolved and absorbed in the metal to form solid solutions within the metal, carbon atoms are then segregated from the solid solution

upon cooling step to the reduction of carbon solubility as temperature reduces, and precipitated (or surface segregated) on the metal surface to form graphene crystals due to the catalytic effect of the metal surface. Here the term "segregation" refers to the separation of carbon atoms from the solid solution within the metal and the term "precipitation" refers to the diffusion and deposition of carbon atoms on the metal surface, which is also called "surface segregation" and in the scientific literature this also includes the crystallisation of graphene on the metal surfaces. For transition metals with relatively lower carbon solubility, with Cu being a typical representation [46–48], dissolution and segregation of carbon atoms in the metal is less likely to happen or at least is not the dominant mechanism due to the lack of carbon solubility in the metal. Graphene is formed on the metal surface directly from the carbon atoms due to the catalytic effect of the metal. Li et al. [48] have experimentally demonstrated the two growth mechanisms by using carbon isotope labelling for the CVD growth on Ni and Cu, respectively, as shown in Fig. 2. The graphene growth process on Ni is shown in Fig. 2a, where the sequentially introduced carbon isotope labels are randomly mixed up in the dissolution and surface segregation process as a result of the dissolution of all carbon atoms in Ni, which lead to a random distribution of the isotope labels in the graphene lattice. In contrast, for graphene grown on Cu, as shown in Fig. 2b, the carbon isotopes in the graphene lattice are distributed in groups, which indicates no dissolution phase in Cu, otherwise the isotope labels would have been randomly mixed up and lead to a random distribution of the isotope labels in graphene, as those shown in Fig. 2a for Ni.

The key parameters for producing better quality graphene include gas concentration/flow rate [79], annealing time/temperature [52], metal grain size [80, 81] and cooling rate [54]. However, the relative importance of these parameters may vary depending on the growth mechanisms. Growth of graphene via the first mechanism tends to form more layers of graphene particularly at the grain boundaries or areas with smaller grains due to the excessive surface segregation or precipitation of carbon on the metal surface. The fast cooling rate is an effective means of obtaining fewer layers or monolayer of graphene [17, 54, 55]. In contrast, longer annealing time is required to form a complete surface coverage of graphene via the second mechanism [46–48]. The growth process is believed to be self-limiting, i.e. no more graphene layers would grow once the metal surface is completely covered by a monolayer graphene as the surface ceases to act as a catalyst (bilayer graphene is obtained instead of monolayer in atmospheric pressure [82]). Cu and Ni are the two
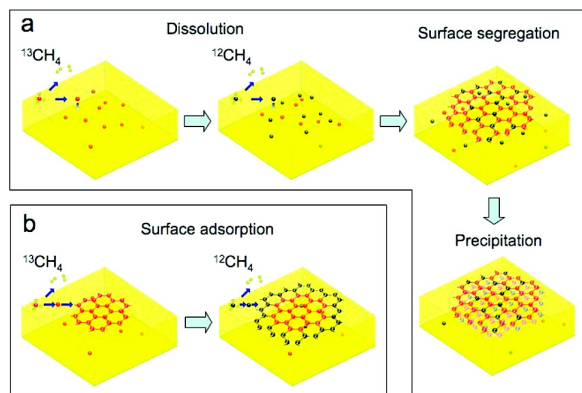
**Figure 2:** Schematic illustration of the two different growth mechanisms in CVD graphene growth, distinguishable by the sequential introduction of carbon isotope labelling during growth. (a), Growth process on Ni, which involves hydrocarbon decomposition - carbon dissolution in Ni – surface segregation of carbon atoms – precipitation of graphene, where the sequential isotope labels were randomly mixed up by the carbon dissolution process because of the carbon high solubility in Ni, led to randomly distributed isotope labels in the graphene lattice. (b), Growth process on Cu, where graphene is grown directly from decomposed carbon atoms on the Cu surface, led to grouped distribution of carbon isotope labels in the graphene lattice, an indication of the non-existence of the carbon dissolution phase because of the very low carbon solubility of Cu. Courtesy of Li et al. [48].

most studied metals for CVD graphene growth. The results so far indicate that the growth on Cu produces better quality of graphene films. For example a 95% surface coverage of monolayer graphene on Cu has been achieved and the mobility of graphene at room temperature can be as high as $10^4$ cm$^{-2}$/V·s [46–48] and crystallite sizes up to ~2 mm [83, 84].
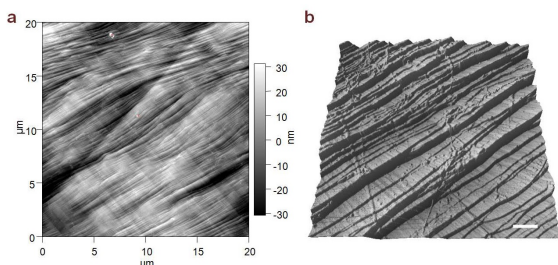


**Figure 3:** Typical surface morphologies of CVD graphene on Cu substrate. 2D AFM image (a) and 3D AFM image (b), showing the inherent nonflat topography with roughness from 3-6 nm. Scale bar in (b): 500 nm. Courtesy of Ruiz-Vargas et al. [85].

The study of surface morphologies of CVD graphene is quite scarce in the literatures. According to the very few papers published, graphene grown on the Cu surface could
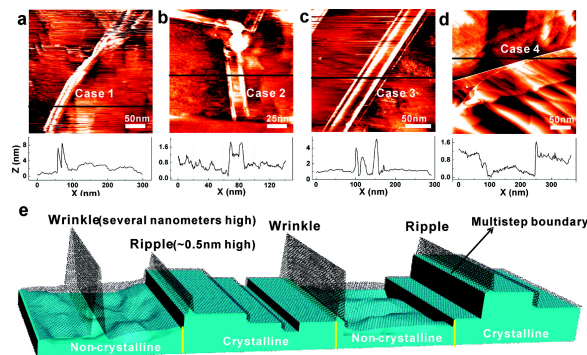


**Figure 4:** STM morphology of graphene on Cu substrate with different Cu crystalline states [86]. (a), STM image of crooked wrinkles on amorphous Cu substrate and its height profile. (b) and (c), Striped ripples and wrinkles evolving along the boundaries from crystalline to non-crystalline states. (d), Ripples appearing on step boundaries of crystalline Cu. (e), Sketch map showing the positions of wrinkles and ripples with substrate states.
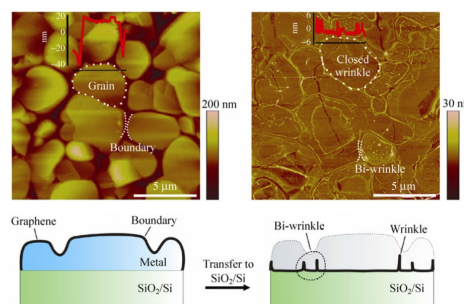


**Figure 5:** AFM images and surface line profile of CVD graphene grown on Ni/SiO$_2$ stack, before and after transfer, respectively. The dotted circle on the top-left image refers to an isolated Ni grain while two adjacent lines correspond to a boundary formed between two Ni grains. The dotted circle and the two adjacent dotted lines on the top-right AFM image highlight the closed wrinkle and bi-wrinkle after transfer, respectively. Bottom line profiles illustrate the surface-topography-preserved after transfer of graphene from a corrugated metal substrate to SiO$_2$/Si substrate. Courtesy of Liu et al. [87].

never be atomically flat [85, 87, 88]. Typical AFM images of graphene morphology on Cu foil are shown in Fig. 3. The terrace and rippling topography of graphene with a typical rms value ranging from 3-6 nm is actually a rubbing of the uneven Cu foil surface underneath, which is due to the inherent nonflat nature of the Cu foil, resulting from the sublimation of Cu and the recrystallization of Cu grains at high processing temperatures. This in turn leads to terraces and ripples once graphene is transferred to SiO$_2$ substrate. Zhang et al. [86] have shown that the non-flat morphology of graphene is also closely related to the difference in thermal expansion coefficients between Cu and graphene, as shown in Fig. 4. Compared with well crys-

tallized Cu foil, the amorphous or transition status Cu foil has a greater difference in thermal expansion coefficient to graphene, resulting in bigger contraction of Cu foil during thermal quenching, which in turn creates higher wrinkles on graphene film. However, graphene grown on well crystallized Cu foil tends to show flat morphology on the top of each terrace but present lower ripples (0.5 nm high) or wrinkles at step areas, which may due to the smaller difference in thermal expansion coefficient to graphene. Liu and co-workers [87] have shown that graphene grown on Ni substrate shows similar problems with that grown on Cu, except that there is no rippling morphology caused by metal sublimation because of the much weaker sublimation of Ni film at graphene growth temperature. A typical AFM image of as-grown graphene on Ni film and its corresponding transferred graphene on $SiO_2$ are shown in Fig. 5. It can be seen that graphene also has a morphology due to rubbing of Ni film underneath, which more or less wraps around hemispherical Ni grains and forms deep trenches between adjacent grains. Once the Ni film is removed, hemispherical graphene falls onto substrate as there is no physical support, resulting in single wrinkles around hemispherical graphene grains and bi-wrinkles between two adjacent hemispherical graphene grains, respectively. It is worth noting that graphene grains here are replicas of Ni grains instead of graphene crystal grains and the wrinkles caused by the difference in thermal expansion coefficient are a few times larger than that caused by Ni recrystallization.

As CVD graphene is grown on top of the transition metal films, it is necessary to transfer the graphene to an insulating substrate, such as Si wafers with a $SiO_2$ insulation layer [49, 55, 89–91] or PET (Polyethylene terephthalate) substrate [92, 93], in order to carry out the electrical characterization of the graphene films and for electronic applications. So far, the PMMA based transfer technique is used extensively in laboratories for research purposes. As-grown graphene sample is spin-coated by PMMA layer and then immersed in certain etchants to remove the metal layer on which graphene is grown. Once the removal of metal layer is completed, the floating graphene/PMMA layer on the etchant surface can be picked up by arbitrary substrate without introducing any visible damage [17], which is due to the hydrophobicity and mechanical strength of graphene. Roll to roll transfer [90] has been achieved and industrially used to produce high quality and large area graphene on PET/epoxy films for applications including touch careen displays [92], flexible heaters [94], solar cells [95, 96], etc. By a combination of Joule heating, CVD growth, gravure coating, UV bonding and spray etching, 100 m long high quality graphene sheet on PET/epoxy substrate has recently been reported by Sony [88]. Further recent developments of the CVD method include the growth of large area high quality graphene by using metal alloy, such as Ni-Cu alloy [97], Ni-Au [98] alloy or Ni-Mo [99, 100].

# 4 Growth from Solid Carbon Sources

In parallel to CVD growth, techniques for the growth of graphene on metal surfaces from solid carbon sources have also been developed. The basic growth mechanism of this approach is as same as that of CVD growth, which uses polycrystalline transition metal films, such as Ni [101], Cu [102] or Co [53] deposited in vacuum as catalyst for the growth of graphene. However, solid carbon-containing films, typically amorphous SiC or C, are used as carbon source and the samples are annealed in a rapid thermal processor (RTP) in either vacuum, Ar or $Ar/H_2$ atmosphere at temperatures up to 1100 °C. Both the metal and C-containing films are deposited on Si wafers by physical vapor deposition such as sputtering [103, 104], evaporation [105], vacuum arc [106], MBE [107] or ion implantation [108, 109]. Spin-coated PMMA [102] or other C-containing materials such as PAN [110], SAM [111], PS [112], PPMS [113], ABS [114], are also used. Carbon impurities contained within the metal or alloy targets are also successfully used as a carbon source for the growth of graphene without the need for an additional carbon source [115]. As the graphene grown by this method is in general on top of the metal layers, it also needs to be transferred to an insulating substrate after growth similar to the CVD graphene method.

This approach was pioneered by Juang et al. [101] using a Ni film deposited by e-beam evaporation on single crystal SiC substrate, where growth of graphene was achieved at RTP temperature of 750 °C, much lower temperature than that for the epitaxial growth. Graphene grown from PECVD-deposited amorphous SiC and sputtered Ni films was also reported in the same year by Hofrichter et al. [116]. In this case, RTP temperature as high as 1100 °C was used. Growth of wafer-scale graphene from solid carbon source has subsequently been demonstrated from a number of layer combinations, such as Ni/SiC [117, 118], Ni/C [104, 106], Ni/PMMA [105, 113, 119], Cu/PMMA [102, 120], NiCu/C [121, 122]. One of the key process parameters for obtaining high quality graphene is the fast cooling rate. Under the optimized process conditions, the quality of graphene appears to be mainly

dependent on the size of grains of the polycrystalline metal film although carbon contents and layer combination may also have some role to play. Monolayer graphene is usually obtained from areas with large grains whilst few layer graphene is observed from areas with smaller grains and grain boundaries. It is therefore arguable that the graphene growth on each metal grain may still be self-limiting and the multilayer nature of the resultant graphene may be caused by the overlapped metal grains which produce overlapped graphene layers [118]. Due to the polycrystalline nature of the metal films, it is in general very challenging to obtain uniform graphene across large areas.

# 5 Transfer-free and Direct Growth on Insulating Substrates

One of the essential requirements for electronic device applications is that graphene must be grown on insulating substrates. As mentioned earlier, this is not possible for CVD growth or growth with solid carbon sources. In order for the graphene grown by these techniques to be used for device applications, a post-growth transfer of graphene from the metal surface to an insulating substrate is required, which is not cost-efficient and likely to introduce contamination or damage the graphene films. This brought about the latest development of graphene growth techniques: transfer-free growth [118] and direct growth [110] of graphene on insulating substrates.

Two different approaches have been reported for the transfer-free growth of graphene: complete evaporation of the supporting metal film after the growth of graphene [73, 123] and etching of the supporting metal film after growth [118]. The "evaporation method" takes advantage of the reduced sublimation temperature of the metal film in vacuum and results in graphene sheet grown atop of metal film to fall onto dielectric surface after the evaporation of metal film. Ariel Ismach et al. [73] first reported this technique in a CVD process. After a very long evaporation process ranging from 15 minutes to 7 hours at 1000 °C and low pressure (100-500mTorr), metal film on top of substrate can be evaporated or dewetted into finger-like structures, leaving inhomogenous graphene on the substrate. The resultant graphene device on $SiO_2$ substrate shows p-type doped behaviour with a mobility of 655 $cm^2V^{-1}s^{-1}$ and a gate modulation of around 3. For the latter approach, Pan et al. [118] have achieved transfer-free growth of graphene from sputtered C/Ni films by applying the diffusion-segregation growth method with a care-

fully designed C/metal thickness. When the Ni thickness is >100 nm, monolayer graphene grows on relatively large Ni grains and floats off after the removal of Ni layer as there is no physical connection between graphene and the substrate, as shown in Fig. 6a. However, when the Ni thickness is <100 nm, graphene grew down to the substrate due to the recrystallization and dewetting of the Ni grains, linking up graphene with the nc-G layer on the substrate so that it retains the original morphology of Ni layer, as shown in Fig. 6b and c. The resultant graphene device presents a same p-type doped characteristic with a mobility of around $10^3$ $cm^2V^{-1}s^{-1}$, but a lower modulation of 1.3. Similar method has since been reported by Gao et al. [124]. By pre-treatment of the substrate with nitrogen plasma, bubble seeds can be planted in the $SiO_2$ layer, which then generate bubbles during the chemical etching process. These resultant bubbles can join those trapped under the graphene film and act together as capillary bridges with a strong negative pressure, resulting in the graphene remaining on the original substrate after the removal of the Cu layer [124]. In this case, the graphene obtained is weakly n-type doped and shows a carrier mobility of 3800 $cm^2V^{-1}s^{-1}$, which is comparable to the properties of CVD graphene.
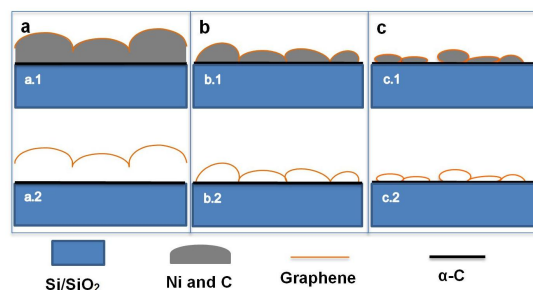


**Figure 6:** Schematic illustration of the growth model. (a) Thick Ni layer (>100 nm) with large grains: graphene grows atop of the stack and replicates the grain morphology of Ni and an nc-G layer is also formed at the interface of Ni and $SiO_2$ (a.1). A floating monolayer graphene sheet (a rigid imprint of the Ni topography) is obtained after the removal of Ni in acid (a.2). (b) Thin Ni layer (30–100 nm): graphene atop of the stack can grow through the grain boundaries and link up with the nc-G layer on the substrate surface (b.1). Graphene remains on the original substrate as a rigid imprint of the Ni topography when the Ni is removed in acid (b.2). (c) Small Ni grains in grain boundaries: monolayer graphene also grows around these small Ni grains (c.1). The resultant graphene sheet has overlapped grains across the grain boundaries due to the irregular grain structures of the Ni (c.2). Courtesy of Pan et al. [118].

Although the metal/$SiO_2$ interface is believed to be chemically unfavourable for the formation of

graphene [118], direct growth of graphene on $SiO_2$ substrate has been reported by a few groups. Byun et al. have obtained graphene directly on the $SiO_2$ substrate using 10nm spin-coated polymer layer as carbon source (PS, PAN or PMMA) and 50 nm Ni layer as buffer, catalyst and capping layer. With RTP at 1000 °C for 1 min, few-layer graphene was obtained directly on $SiO_2$ substrate [110]. The quality of graphene varies with different carbon sources used. A few more groups have also reported similar results by using different carbon source and transition metal film/alloy combinations, such as $CH_4$/Cu, ABS/Ni, SAM/Ni or Cu/Ni(containing trace amorphous carbon) [16, 113, 119, 122]. By tuning the process parameters, low-defect graphene with a bilayer coverage $\sim$70% and a monolayer coverage $\sim$20% of the wafer can be obtained on the $SiO_2$ substrate. The most important advantage of this method is that graphene forms directly on the atomically flat substrate surface although the quality of the graphene film is still far from desirable. The major problems encountered in the growth process are the carbon atoms favour segregating through metal grain boundaries or micro voids of metal layer (shown in Fig. 7a [16, 125]), resulting in ridges on the graphene film (shown in Fig. 7b). The Raman spectrum taken from the ridge area shows a relatively high D band and G/2D intensity ratio (shown in Fig. 7c), which confirms that the graphene around the ridges presents greater defects and more layers and the resultant devices produced by this graphene always show a low mobility ranging from 150-700 $cm^2V^{-1}s^{-1}$ as well as heavily p-doped characteristic.
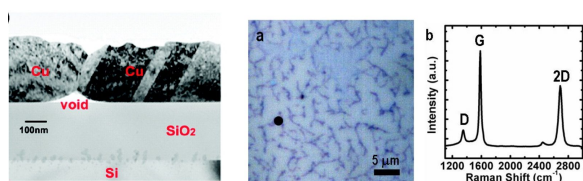


**Figure 7:** TEM, optical images and Raman spectrum of graphene grown at the metal/$SiO_2$ interface. (a), cross-sectional TEM image shows grain boundary and void. (b), Optical microscope image of graphene ridges in the sample grown at T = 160 °C for 2 min on $SiO_2$. The morphology of graphene ridges reflects the grain boundaries in poly-Ni films. c, Typical Raman spectra acquired from a ridge highlighted by a black dot in b, showing the D, G, and 2D peaks at peak positions expected for graphene. Courtesy of Su et al. [16] and Jinshuang et al. [125].

For both transfer-free and direct growth on insulating or dielectric substrate, the most important parameter is the thickness of metal film or the ratio of carbon source/metal, because of the diffusion-segregation growth

mechanism. The use of an overly thick metal layer, i.e., a low carbon to metal ratio, leads to a low coverage of graphene or the loss of the physical connections between graphene and substrate. However, an overly thin metal layer, i.e., a high carbon to metal ratio, can cause dewetting of the metal film before graphene growth or excessive segregation of amorphous carbon after the growth of first few layers of graphene.

Growth of graphene without requiring catalyst metal layer was first reported by Zhang and his co-workers [126], in which remote plasma enhancement chemical vapour deposition (r-PECVD) was successfully employed for the growth of wafer-scale graphene on various insulating substrates. Direct growth of large scale monolayer graphene by CVD on Ge substrate was pioneered by Wang and his co-workers very recently [127]. Carbon containing radicals were introduced into the growth chamber with temperatures ranging from 800-910 °C and a $H_2$/$CH_4$ ratio of 50:0.1, where they were adsorbed onto Ge substrate and interlinked to each other by collision, leading to the formation and extension of graphene nano-clusters. Under optimum growth conditions, homogeneous monolayer graphene was grown directly on Ge substrates over a large scale. The positively shifted Dirac point can be observed together with a mobility of 800-900 $cm^2V^{-1}s^{-1}$ from its resultant FET device, which is comparable to that reported from transferred CVD graphene. By using the same method but a hydrogen terminated Ge (110) substrate, wafer-scale growth of wrinkle-free single-crystal monolayer graphene has also been achieved [128]. It was believed that the anisotropic atomic arrangement of single crystal Ge substrate enables unidirectional alignment of graphene seeds merging into graphene sheet with same orientation. Compared with polycrystalline graphene grown from Ge, a much higher mobility up to $\sim$$10^4$ $cm^2V^{-1}s^{-1}$ was recorded due to the absence of defective grain boundaries and wrinkles which always lead to scattering. The process is believed to be self-limiting due to the incredibly low solubility of C in Ge under equilibrium conditions.

# 6 Conclusions and Prospects

Since the discovery of graphene in 2004, a number of techniques for the production of large area graphene have been developed. Epitaxial growth from single crystal SiC substrate offers an industrial scale growth method for large area graphene directly on semi-insulating substrates with the potential for electronic devices applications without the need of transfer. However, its indus-

trial scale production is constrained by the high cost of both the substrate material and the very high growth temperatures (>1200 °C). The non-flat terraced morphology is another limitation. Growth of graphene via chemical vapour deposition on transition metal films, particularly on Cu sheets or films, is a promising production method. As the graphene can be transferred to any substrate, although it's not defect-free, it has been employed for a wide range of applications, particularly as transparent conducting coatings for applications in touch screen displays, e-paper (electronic paper) and organic light-emitting diodes (OLEDs). Although cheaper than epitaxial growth, the CVD method is still a high energy consumption process due to its high growth temperature. The need to etch away the Cu sheets also makes the process expensive. Further improvements of the method include the use of very thin Cu films without sacrificing the crystal size, quality and properties of graphene. Growth from solid carbon source and transfer free growth are other interesting developments for the production of large area graphene although further improvements of these processes is needed to make them viable for industrial scale device applications. Each technique developed so far has its own advantages and limitations, and are still far from meeting the requirements for realising the industrial scale applications of graphene. Although it is unlikely that graphene will be employed in the near future for applications in high-performance digital circuits because of the absence of a bandgap, the other superior electron transport properties of graphene have the potential to make the material a promising candidate for applications in analogue electronics and sensors. The main challenge for realizing such a potential is the development of wafer scale production technique for atomically flat and defect-free single crystal graphene directly on Si insulating substrates. The development of such a production technique for graphene would represent a major advance [129] towards the realization of the graphene revolution.

# References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, *et al.*, "Electric Field Effect in Atomically Thin Carbon Films," *Science,* vol. 306, pp. 666-669, October 22, 2004 2004.

[2] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nat Mater,* vol. 6, pp. 183-191, 2007.

[3] AlexanderAlUS. (2010). *The ideal crystalline structure of graphene is a hexagonal grid.* Available: http://en.wikipedia.org/wiki/File:Graphen.jpg

[4] K. Seibert, G. C. Cho, W. Kütt, H. Kurz, D. H. Reitze, M. C. Downer, *et al.*, "Ultrafast Relaxation Processes of Hot Carriers in Graphite," in *Ultrafast Phenomena VII*. vol. 53, C. Harris, E. Ippen, G. Mourou, and A. Zewail, Eds., ed: Springer Berlin Heidelberg, 1990, pp. 303-305.

[5] K. Andre and K. Philip, "Carbon Wonderland," *Scientific American,* vol. 298, pp. 90-97, 2008.

[6] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, *et al.*, "Ultrahigh electron mobility in suspended graphene," *Solid State Communications,* vol. 146, pp. 351-355, 2008.

[7] J.-H. Chen, C. Jang, S. Xiao, M. Ishigami, and M. S. Fuhrer, "Intrinsic and extrinsic performance limits of graphene devices on $SiO_2$," *Nat Nano,* vol. 3, pp. 206-209, 2008.

[8] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, *et al.*, "Two-dimensional gas of massless Dirac fermions in graphene," *Nature,* vol. 438, pp. 197-200, 11/10/print 2005.

[9] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, "The electronic properties of graphene," *Reviews of Modern Physics,* vol. 81, p. 109, 2009.

[10] Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, "Experimental observation of the quantum Hall effect and Berry's phase in graphene," *Nature,* vol. 438, pp. 201-204, 2005.

[11] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, *et al.*, "Two-dimensional atomic crystals," *Proceedings of the National Academy of Sciences of the United States of America,* vol. 102, pp. 10451-10453, July 26, 2005 2005.

[12] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, *et al.*, "Electronic Confinement and Coherence in Patterned Epitaxial Graphene," *Science,* vol. 312, pp. 1191-1196, May 26, 2006 2006.

[13] T. Ohta, A. Bostwick, T. Seyller, K. Horn, and E. Rotenberg, "Controlling the Electronic Structure of Bilayer Graphene," *Science,* vol. 313, pp. 951-954, August 18, 2006 2006.

[14] C. Jia, J. Jiang, L. Gan, and X. Guo, "Direct Optical Characterization of Graphene Growth and Domains on Growth Substrates," *Sci. Rep.,* vol. 2, 2012.

[15] C. Lee, X. Wei, J. W. Kysar, and J. Hone, "Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene," *Science,* vol. 321, pp. 385-388, July 18, 2008 2008.

[16] C.-Y. Su, A.-Y. Lu, C.-Y. Wu, Y.-T. Li, K.-K. Liu, W. Zhang, *et al.*, "Direct Formation of Wafer Scale Graphene Thin Layers on Insulating Substrates by Chemical Vapor Deposition," *Nano Letters,* vol. 11, pp. 3612-3616, 2011/09/14 2011.

[17] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, *et al.*, "Large-scale pattern growth of graphene films for stretchable transparent electrodes," *Nature,* vol. 457, pp. 706-710, 2009.

[18] H. J. Park, J. Meyer, S. Roth, and V. Skákalová, "Growth and properties of few-layer graphene prepared by chemical vapor deposition," *Carbon,* vol. 48, pp. 1088-1094, 2010.

[19] N. Tombros, C. Jozsa, M. Popinciuc, H. T. Jonkman, and B. J. van Wees, "Electronic spin transport and spin precession in single graphene layers at room temperature," *Nature,* vol. 448, pp.

571-574, 2007.

[20] X. Wang, X. Li, L. Zhang, Y. Yoon, P. K. Weber, H. Wang, *et al.*, "N-Doping of Graphene Through Electrothermal Reactions with Ammonia," *Science,* vol. 324, pp. 768-771, May 8, 2009 2009.

[21] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, *et al.*, "Ultrathin Epitaxial Graphite: 2D Electron Gas Properties and a Route toward Graphene-based Nanoelectronics," *The Journal of Physical Chemistry B,* vol. 108, pp. 19912-19916, 2004/12/01 2004.

[22] B. Guo, Q. Liu, E. Chen, H. Zhu, L. Fang, and J. R. Gong, "Controllable N-Doping of Graphene," *Nano Letters,* vol. 10, pp. 4975-4980, 2010/12/08 2010.

[23] F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, "Graphene photonics and optoelectronics," *Nat Photon,* vol. 4, pp. 611-622, 2010.

[24] J. Wu, H. A. Becerril, Z. Bao, Z. Liu, Y. Chen, and P. Peumans, "Organic solar cells with solution-processed graphene transparent electrodes," *Applied Physics Letters,* vol. 92, pp. -, 2008.

[25] Q. Lu, X. Dong, L.-J. Li, and X. Hu, "Direct electrochemistry-based hydrogen peroxide biosensor formed from single-layer graphene nanoplatelet–enzyme composite film," *Talanta,* vol. 82, pp. 1344-1348, 2010.

[26] N. Mohanty and V. Berry, "Graphene-Based Single-Bacterium Resolution Biodevice and DNA Transistor: Interfacing Graphene Derivatives with Nanoscale and Microscale Biocomponents," *Nano Letters,* vol. 8, pp. 4469-4476, 2008/12/10 2008.

[27] M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, "Graphene-Based Ultracapacitors," *Nano Letters,* vol. 8, pp. 3498-3502, 2008/10/08 2008.

[28] Y.-W. Son, M. L. Cohen, and S. G. Louie, "Half-metallic graphene nanoribbons," *Nature,* vol. 444, pp. 347-349, 2006.

[29] B. Trauzettel, D. V. Bulaev, D. Loss, and G. Burkard, "Spin qubits in graphene quantum dots," *Nat Phys,* vol. 3, pp. 192-196, 2007.

[30] T. Yokoyama, "Controllable spin transport in ferromagnetic graphene junctions," *Physical Review B,* vol. 77, p. 073413, 2008.

[31] V. Fal'ko, "Graphene: Quantum information on chicken wire," *Nat Phys,* vol. 3, pp. 151-152, 2007.

[32] F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, and A. C. Ferrari, "Production and processing of graphene and 2d crystals," *Materials Today,* vol. 15, pp. 564-589, 12// 2012.

[33] A. J. Van Bommel, J. E. Crombeen, and A. Van Tooren, "LEED and Auger electron observations of the SiC(0001) surface," *Surface Science,* vol. 48, pp. 463-472, 1975.

[34] I. Forbeaux, J. M. Themlin, A. Charrier, F. Thibaudau, and J. M. Debever, "Solid-state graphitization mechanisms of silicon carbide 6H−SiC polar faces," *Applied Surface Science,* vol. 162–163, pp. 406-412, 2000.

[35] I. Forbeaux, J. M. Themlin, and J. M. Debever, "Heteroepitaxial graphite on 6H-SiC(0001): Interface formation through conduction-band electronic structure," *Physical Review B,* vol. 58, pp. 16396-16406, 1998.

[36] P. Sutter, "Epitaxial graphene: How silicon leaves the scene," *Nat Mater,* vol. 8, pp. 171-172, 2009.

[37] W. A. de Heer, C. Berger, X. Wu, P. N. First, E. H. Conrad, X. Li, *et al.*, "Epitaxial graphene," *Solid State Communications,* vol. 143, pp. 92-100, 2007.

[38] N. Srivastava, H. Guowei, Luxmi, P. C. Mende, R. M. Feenstra, and S. Yugang, "Graphene formed on SiC under various environments: comparison of Si-face and C-face," *Journal of Physics D: Applied Physics,* vol. 45, p. 154001, 2012.

[39] K. V. Emtsev, T. Seyller, L. Ley, A. Tadich, L. Broekman, J. D. Riley, *et al.*, "Electronic properties of clean unreconstructed 6H−SiC(0 0 0 1) surfaces studied by angle resolved photoelectron spectroscopy," *Surface Science,* vol. 600, pp. 3845-3850, 2006.

[40] K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, *et al.*, "Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide," *Nat Mater,* vol. 8, pp. 203-207, 2009.

[41] C. Riedl, C. Coletti, and U. Starke, "Structural and electronic properties of epitaxial graphene on SiC(0?0?0?1): a review of growth, characterization, transfer doping and hydrogen intercalation," *Journal of Physics D: Applied Physics,* vol. 43, p. 374009, 2010.

[42] G. G. Jernigan, B. L. VanMil, J. L. Tedesco, J. G. Tischler, E. R. Glaser, A. Davidson, *et al.*, "Comparison of Epitaxial Graphene on Si-face and C-face 4H SiC Formed by Ultrahigh Vacuum and RF Furnace Production," *Nano Letters,* vol. 9, pp. 2605-2609, 2009/07/08 2009.

[43] F. Schwierz, "Graphene transistors," *Nat Nano,* vol. 5, pp. 487-496, 2010.

[44] Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, *et al.*, "100-GHz Transistors from Wafer-Scale Epitaxial Graphene," *Science,* vol. 327, p. 662, February 5, 2010 2010.

[45] Y.-M. Lin, A. Valdes-Garcia, S.-J. Han, D. B. Farmer, I. Meric, Y. Sun, *et al.*, "Wafer-Scale Graphene Integrated Circuit," *Science,* vol. 332, pp. 1294-1297, June 10, 2011 2011.

[46] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, *et al.*, "Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils," *Science,* vol. 324, pp. 1312-1314, June 5, 2009 2009.

[47] Y. Lee, S. Bae, H. Jang, S. Jang, S.-E. Zhu, S. H. Sim, *et al.*, "Wafer-Scale Synthesis and Transfer of Graphene Films," *Nano Letters,* vol. 10, pp. 490-493, 2010/02/10 2010.

[48] X. Li, W. Cai, L. Colombo, and R. S. Ruoff, "Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling," *Nano Letters,* vol. 9, pp. 4268-4272, 2009/12/09 2009.

[49] S. Lee, K. Lee, and Z. Zhong, "Wafer Scale Homogeneous Bilayer Graphene Films by Chemical Vapor Deposition," *Nano Letters,* vol. 10, pp. 4702-4707, 2010/11/10 2010.

[50] C. Vo-Van, A. Kimouche, A. Reserbat-Plantey, O. Fruchart, P. Bayle-Guillemaud, N. Bendiab, *et al.*, "Epitaxial graphene prepared by chemical vapor deposition on single crystal thin iridium films on sapphire," *Applied Physics Letters,* vol. 98, p. 181903, 2011.

[51] Y. Miyasaka, A. Nakamura, and J. Temmyo, "Graphite Thin Films Consisting of Nanograins of Multilayer Graphene on Sapphire Substrates Directly Grown by Alcohol Chemical Vapor Deposition," *Japanese Journal of Applied Physics,* vol. 50, p. 04DH12, 2011.

[52] G. Alexander, K. Kurt, and V. V. Denis, "Dynamics of graphene growth on a metal surface: a time-dependent photoemission study," *New Journal of Physics,* vol. 11, p. 073050, 2009.

[53] M. E. Ramón, A. Gupta, C. Corbet, D. A. Ferrer, H. C. P. Movva, G. Carpenter, *et al.*, "CMOS-Compatible Synthesis of Large-Area, High-Mobility Graphene by Chemical Vapor Deposition

of Acetylene on Cobalt Thin Films," *ACS Nano,* vol. 5, pp. 7198-7204, 2011/09/27 2011.

[54] Q. Yu, J. Lian, S. Siriponglert, H. Li, Y. P. Chen, and S.-S. Pei, "Graphene segregated on Ni surfaces and transferred to insulators," *Applied Physics Letters,* vol. 93, p. 113103, 2008.

[55] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, *et al.*, "Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition," *Nano Letters,* vol. 9, pp. 30-35, 2009/01/14 2008.

[56] P. W. Sutter, J.-I. Flege, and E. A. Sutter, "Epitaxial graphene on ruthenium," *Nat Mater,* vol. 7, pp. 406-411, 2008.

[57] E. Sutter, P. Albrecht, and P. Sutter, "Graphene growth on polycrystalline Ru thin films," *Applied Physics Letters,* vol. 95, p. 133109, 2009.

[58] P. W. Sutter, P. M. Albrecht, and E. A. Sutter, "Graphene growth on epitaxial Ru thin films on sapphire," *Applied Physics Letters,* vol. 97, p. 213101, 2010.

[59] J. Coraux, A. T. N'Diaye, C. Busse, and T. Michely, "Structural Coherency of Graphene on Ir(111)," *Nano Letters,* vol. 8, pp. 565-570, 2008/02/01 2008.

[60] T. Oznuluer, E. Pince, E. O. Polat, O. Balci, O. Salihoglu, and C. Kocabas, "Synthesis of graphene on gold," *Applied Physics Letters,* vol. 98, pp. 183101-183101-3, 2011.

[61] B. J. Kang, J. H. Mun, C. Y. Hwang, and B. J. Cho, "Monolayer graphene growth on sputtered thin film platinum," *Journal of Applied Physics,* vol. 106, p. 104309, 2009.

[62] E. V. Rut'kov, A. V. Kuz'michev, and N. R. Gall', "Carbon interaction with rhodium surface: Adsorption, dissolution, segregation, growth of graphene layers," *Physics of the Solid State,* vol. 53, pp. 1092-1098, 2011/05/01 2011.

[63] S. Roth, J. Osterwalder, and T. Greber, "Synthesis of epitaxial graphene on rhodium from 3-pentanone," *Surface Science,* vol. 605, pp. L17-L19, 2011.

[64] S.-Y. Kwon, C. V. Ciobanu, V. Petrova, V. B. Shenoy, J. Bareño, V. Gambin, *et al.*, "Growth of Semiconducting Graphene on Palladium," *Nano Letters,* vol. 9, pp. 3985-3990, 2009/12/09 2009.

[65] Y. Murata, S. Nie, A. Ebnonnasir, E. Starodub, B. B. Kappes, K. F. McCarty, *et al.*, "Growth structure and work function of bilayer graphene on Pd(111)," *Physical Review B,* vol. 85, p. 205443, 2012.

[66] H. An, W.-J. Lee, and J. Jung, "Graphene synthesis on Fe foil using thermal CVD," *Current Applied Physics,* vol. 11, pp. S81-S85, 2011.

[67] P. R. Somani, S. P. Somani, and M. Umeno, "Planer nanographenes from camphor by CVD," *Chemical Physics Letters,* vol. 430, pp. 56-59, 2006.

[68] J. H. Hafner, C. L. Cheung, and C. M. Lieber, "Growth of nanotubes for probe microscopy tips," *Nature,* vol. 398, pp. 761-762, 1999.

[69] T. Land, T. Michely, R. Behm, J. Hemminger, and G. Comsa, "STM investigation of single layer graphite structures produced on Pt (111) by hydrocarbon decomposition," *Surface Science,* vol. 264, pp. 261-270, 1992.

[70] A. Nagashima, K. Nuka, H. Itoh, T. Ichinokawa, C. Oshima, and S. Otani, "Electronic states of monolayer graphite formed on TiC (111) surface," *Surface Science,* vol. 291, pp. 93-98, 1993.

[71] Z. Li, P. Wu, c. Wang, X. Fan, W. Zhang, X. Zhai, *et al.*, "Chemical Vapor Deposition Growth of Graphene using Other Hydrocarbon Sources," 2011.

[72] X. Li, C. W. Magnuson, A. Venugopal, J. An, J. W. Suk, B. Han, *et al.*, "Graphene Films with Large Domain Size by a Two-Step Chemical Vapor Deposition Process," *Nano Letters,* vol. 10, pp. 4328-4334, 2010/11/10 2010.

[73] A. Ismach, C. Druzgalski, S. Penwell, A. Schwartzberg, M. Zheng, A. Javey, *et al.*, "Direct Chemical Vapor Deposition of Graphene on Dielectric Surfaces," *Nano Letters,* vol. 10, pp. 1542-1548, 2010/05/12 2010.

[74] L. G. De Arco, Z. Yi, A. Kumar, and Z. Chongwu, "Synthesis, Transfer, and Devices of Single- and Few-Layer Graphene by Chemical Vapor Deposition," *Nanotechnology, IEEE Transactions on,* vol. 8, pp. 135-138, 2009.

[75] J. Hamilton and J. Blakely, "Carbon segregation to single crystal surfaces of Pt, Pd and Co," *Surface Science,* vol. 91, pp. 199-217, 1980.

[76] M. Eizenberg and J. Blakely, "Carbon monolayer phase condensation on Ni (111)," *Surface Science,* vol. 82, pp. 228-236, 1979.

[77] F. Himpsel, K. Christmann, P. Heimann, D. Eastman, and P. J. Feibelman, "Adsorbate band dispersions for C on Ru (0001)," *Surface Science Letters,* vol. 115, pp. L159-L164, 1982.

[78] N. A. Kholin, E. V. Rut'kov, and A. Y. Tontegode, "The nature of the adsorption bond between graphite islands and iridium surface," *Surface Science,* vol. 139, pp. 155-172, 1984.

[79] A. Reina, S. Thiele, X. Jia, S. Bhaviripudi, M. Dresselhaus, J. Schaefer, *et al.*, "Growth of large-area single- and Bi-layer graphene by controlled carbon precipitation on polycrystalline Ni surfaces," *Nano Research,* vol. 2, pp. 509-516, 2009/06/01 2009.

[80] H. Wang, G. Wang, P. Bao, S. Yang, W. Zhu, X. Xie, *et al.*, "Controllable synthesis of submillimeter single-crystal monolayer graphene domains on copper foils by suppressing nucleation," *Journal of the American Chemical Society,* vol. 134, pp. 3627-3630, 2012.

[81] Y. Zhang, L. Gomez, F. N. Ishikawa, A. Madaria, K. Ryu, C. Wang, *et al.*, "Comparison of Graphene Growth on Single-Crystalline and Polycrystalline Ni by Chemical Vapor Deposition," *The Journal of Physical Chemistry Letters,* vol. 1, pp. 3101-3107, 2010/10/21 2010.

[82] Z. Luo, Y. Lu, D. W. Singer, M. E. Berck, L. A. Somers, B. R. Goldsmith, *et al.*, "Effect of Substrate Roughness and Feedstock Concentration on Growth of Wafer-Scale Graphene at Atmospheric Pressure," *Chemistry of Materials,* vol. 23, pp. 1441-1447, 2011/03/22 2011.

[83] C. Wang, W. Chen, C. Han, G. Wang, B. Tang, C. Tang, *et al.*, "Growth of Millimeter-Size Single Crystal Graphene on Cu Foils by Circumfluence Chemical Vapor Deposition," *Sci. Rep.,* vol. 4, 04/01/online 2014.

[84] S. Chen, H. Ji, H. Chou, Q. Li, H. Li, J. W. Suk, *et al.*, "Millimeter-Size Single-Crystal Graphene by Suppressing Evaporative Loss of Cu During Low Pressure Chemical Vapor Deposition," *Advanced Materials,* vol. 25, pp. 2062-2065, 2013.

[85] C. S. Ruiz-Vargas, H. L. Zhuang, P. Y. Huang, A. M. van der Zande, S. Garg, P. L. McEuen, *et al.*, "Softened Elastic Response and Unzipping in Chemical Vapor Deposition Graphene Membranes," *Nano Letters,* vol. 11, pp. 2259-2263, 2011/06/08 2011.

[86] Y. Zhang, T. Gao, Y. Gao, S. Xie, Q. Ji, K. Yan, *et al.*, "Defect-like Structures of Graphene on Copper Foils for Strain Relief Investigated by High-Resolution Scanning Tunneling Microscopy,"

ACS Nano, vol. 5, pp. 4014-4022, 2011/05/24 2011.

[87] N. Liu, Z. Pan, L. Fu, C. Zhang, B. Dai, and Z. Liu, "The origin of wrinkles on transferred graphene," *Nano Research,* vol. 4, pp. 996-1004, 2011/10/01 2011.

[88] T. Kobayashi, M. Bando, N. Kimura, K. Shimizu, K. Kadono, N. Umezu*, et al.*, "Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process," *Applied Physics Letters,* vol. 102, pp. -, 2013.

[89] C. Berger, Z. M. Song, T. B. Li, X. B. Li, A. Y. Ogbazghi, R. Feng, *et al.*, "Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics," *Journal of Physical Chemistry B,* vol. 108, pp. 19912-19916, Dec 30 2004.

[90] Z.-Y. Juang, C.-Y. Wu, A.-Y. Lu, C.-Y. Su, K.-C. Leou, F.-R. Chen*, et al.*, "Graphene synthesis by chemical vapor deposition and transfer by a roll-to-roll process," *Carbon,* vol. 48, pp. 3169-3174, 2010.

[91] A. Reina, H. Son, L. Jiao, B. Fan, M. S. Dresselhaus, Z. Liu*, et al.*, "Transferring and Identification of Single- and Few-Layer Graphene on Arbitrary Substrates," *The Journal of Physical Chemistry C,* vol. 112, pp. 17741-17744, 2008/11/20 2008.

[92] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng*, et al.*, "Roll-to-roll production of 30-inch graphene films for transparent electrodes," *Nat Nano,* vol. 5, pp. 574-578, 2010.

[93] X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen*, et al.*, "Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes," *Nano Letters,* vol. 9, pp. 4359-4363, 2009/12/09 2009.

[94] J. Kang, H. Kim, K. S. Kim, S.-K. Lee, S. Bae, J.-H. Ahn*, et al.*, "High-performance graphene-based transparent flexible heaters," *Nano Letters,* vol. 11, pp. 5154-5158, 2011.

[95] Y.-Y. Lee, K.-H. Tu, C.-C. Yu, S.-S. Li, J.-Y. Hwang, C.-C. Lin*, et al.*, "Top Laminated Graphene Electrode in a Semitransparent Polymer Solar Cell by Simultaneous Thermal Annealing/Releasing Method," *ACS Nano,* vol. 5, pp. 6564-6570, 2011/08/23 2011.

[96] N. Espinosa, R. García-Valverde, A. Urbina, and F. C. Krebs, "A life cycle analysis of polymer solar cell modules prepared using roll-to-roll methods under ambient conditions," *Solar Energy Materials and Solar Cells,* vol. 95, pp. 1293-1302, 2011.

[97] S. Chen, W. Cai, R. D. Piner, J. W. Suk, Y. Wu, Y. Ren*, et al.*, "Synthesis and Characterization of Large-Area Graphene and Graphite Films on Commercial Cu–Ni Alloy Foils," *Nano Letters,* vol. 11, pp. 3519-3525, 2011/09/14 2011.

[98] R. S. Weatherup, B. C. Bayer, R. Blume, C. Ducati, C. Baehtz, R. Schlögl*, et al.*, "In Situ Characterization of Alloy Catalysts for Low-Temperature Graphene Growth," *Nano Letters,* vol. 11, pp. 4154-4160, 2011/10/12 2011.

[99] B. Dai, L. Fu, Z. Zou, M. Wang, H. Xu, S. Wang*, et al.*, "Rational design of a binary metal alloy for chemical vapour deposition growth of uniform single-layer graphene," *Nat Commun,* vol. 2, p. 522, 2011.

[100] Y. S. Woo, D. H. Seo, D.-H. Yeon, J. Heo, H.-J. Chung, A. Benayad*, et al.*, "Low temperature growth of complete monolayer graphene films on Ni-doped copper and gold catalysts by a self-limiting surface reaction," *Carbon,* vol. 64, pp. 315-323, 2013.

[101] Z.-Y. Juang, C.-Y. Wu, C.-W. Lo, W.-Y. Chen, C.-F. Huang, J.-C. Hwang*, et al.*, "Synthesis of graphene on silicon carbide sub-strates at low temperature," *Carbon,* vol. 47, pp. 2026-2031, 2009.

[102] Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu, and J. M. Tour, "Growth of graphene from solid carbon sources," *Nature,* vol. 468, pp. 549-552, 2010.

[103] C. Orofeo, H. Ago, B. Hu, and M. Tsuji, "Synthesis of large area, homogeneous, single layer graphene films by annealing amorphous carbon on Co and Ni," *Nano Research,* vol. 4, pp. 531-540, 2011/06/01 2011.

[104] W. Xiong, Y. S. Zhou, L. J. Jiang, A. Sarkar, M. Mahjouri-Samani, Z. Q. Xie*, et al.*, "Single-Step Formation of Graphene on Dielectric Surfaces," *Advanced Materials,* vol. 25, pp. 630-634, 2013.

[105] M. Zheng, K. Takei, B. Hsia, H. Fang, X. Zhang, N. Ferralis*, et al.*, "Metal-catalyzed crystallization of amorphous carbon to graphene," *Applied Physics Letters,* vol. 96, p. 063110, 2010.

[106] J. H. Seo, H. W. Lee, J.-K. Kim, D.-G. Kim, J.-W. Kang, M.-S. Kang*, et al.*, "Few layer graphene synthesized by filtered vacuum arc system using solid carbon source," *Current Applied Physics,* vol. 12, Supplement 2, pp. S131-S133, 2012.

[107] E. Moreau, F. Ferrer, D. Vignaud, S. Godey, and X. Wallart, "Graphene growth by molecular beam epitaxy using a solid carbon source," *physica status solidi (a),* vol. 207, pp. 300-303, 2010.

[108] L. Baraton, Z. B. He, C. S. Lee, C. S. Cojocaru, M. Châtelet, J. L. Maurice*, et al.*, "On the mechanisms of precipitation of graphene on nickel thin films," *EPL (Europhysics Letters),* vol. 96, p. 46003, 2011.

[109] B. Laurent, H. Zhanbing, L. Chang Seok, M. Jean-Luc, C. Costel Sorin, G.-L. Anne-Françoise*, et al.*, "Synthesis of few-layered graphene by ion implantation of carbon in nickel thin films," *Nanotechnology,* vol. 22, p. 085601, 2011.

[110] S.-J. Byun, H. Lim, G.-Y. Shin, T.-H. Han, S. H. Oh, J.-H. Ahn*, et al.*, "Graphenes Converted from Polymers," *The Journal of Physical Chemistry Letters,* vol. 2, pp. 493-497, 2011/03/03 2011.

[111] H.-J. Shin, W. M. Choi, S.-M. Yoon, G. H. Han, Y. S. Woo, E. S. Kim*, et al.*, "Transfer-Free Growth of Few-Layer Graphene by Self-Assembled Monolayers," *Advanced Materials,* vol. 23, pp. 4392-4397, 2011.

[112] T. Wu, G. Ding, H. Shen, H. Wang, L. Sun, D. Jiang*, et al.*, "Triggering the Continuous Growth of Graphene Toward Millimeter-Sized Grains," *Advanced Functional Materials,* vol. 23, pp. 198-203, 2013.

[113] Z. Yan, Z. Peng, Z. Sun, J. Yao, Y. Zhu, Z. Liu*, et al.*, "Growth of Bilayer Graphene on Insulating Substrates," *ACS Nano,* vol. 5, pp. 8187-8192, 2011/10/25 2011.

[114] G. Lippert, J. Dabrowski, M. Lemme, C. Marcus, O. Seifarth, and G. Lupina, "Direct graphene growth on insulator," *physica status solidi (b),* vol. 248, pp. 2619-2622, 2011.

[115] N. Liu, L. Fu, B. Dai, K. Yan, X. Liu, R. Zhao*, et al.*, "Universal Segregation Growth Approach to Wafer-Size Graphene from Non-Noble Metals," *Nano Letters,* vol. 11, pp. 297-303, 2011/01/12 2010.

[116] J. Hofrichter, B. u. N. Szafranek, M. Otto, T. J. Echtermeyer, M. Baus, A. Majerus*, et al.*, "Synthesis of Graphene on Silicon Dioxide by a Solid Carbon Source," *Nano Letters,* vol. 10, pp. 36-42, 2010/01/13 2009.

[117] C. Y. Kang, L. L. Fan, S. Chen, Z. L. Liu, P. S. Xu, and C. W. Zou, "Few-layer graphene growth on 6H-SiC(0001) surface at low temperature via Ni-silicidation reactions," *Applied Physics Let-*

*ters,* vol. 100, pp. 251604-251604-5, 2012.

[118] G. Pan, B. Li, M. Heath, D. Horsell, M. L. Wears, L. Al Taan, *et al.*, "Transfer-free growth of graphene on $SiO_2$ insulator substrate from sputtered carbon and nickel films," *Carbon,* vol. 65, pp. 349-358, 2013.

[119] Z. Peng, Z. Yan, Z. Sun, and J. M. Tour, "Direct Growth of Bilayer Graphene on $SiO_2$ Substrates by Carbon Diffusion through Nickel," *ACS Nano,* vol. 5, pp. 8241-8247, 2011/10/25 2011.

[120] S. Suzuki, Y. Takei, K. Furukawa, and H. Hibino, "Graphene Growth from a Spin-Coated Polymer without a Reactive Gas," *Applied Physics Express,* vol. 4, 2011.

[121] X. Liu, L. Fu, N. Liu, T. Gao, Y. Zhang, L. Liao, *et al.*, "Segregation Growth of Graphene on Cu–Ni Alloy for Precise Layer Control," *The Journal of Physical Chemistry C,* vol. 115, pp. 11976-11982, 2011/06/23 2011.

[122] H. Sojoudi and S. Graham, "Transfer-Free Selective Area Synthesis of Graphene Using Solid-State Self-Segregation of Carbon In Cu/Ni Bilayers," *ECS Journal of Solid State Science and Technology,* vol. 2, pp. M17-M21, January 1, 2013 2013.

[123] D. Wang, H. Tian, Y. Yang, D. Xie, T.-L. Ren, and Y. Zhang, "Scalable and Direct Growth of Graphene Micro Ribbons on Dielectric Substrates," *Sci. Rep.,* vol. 3, 2013.

[124] L. Gao, G.-X. Ni, Y. Liu, B. Liu, A. H. Castro Neto, and K. P. Loh, "Face-to-face transfer of wafer-scale graphene films," *Nature,* vol. advance online publication, 2013.

[125] J. Kwak, J. H. Chu, J.-K. Choi, S.-D. Park, H. Go, S. Y. Kim, *et al.*, "Near room-temperature synthesis of transfer-free graphene films," *Nat Commun,* vol. 3, p. 645, 2012.

[126] L. Zhang, Z. Shi, Y. Wang, R. Yang, D. Shi, and G. Zhang, "Catalyst-free growth of nanographene films on various substrates," *Nano Research,* vol. 4, pp. 315-321, 2011.

[127] G. Wang, M. Zhang, Y. Zhu, G. Ding, D. Jiang, Q. Guo, *et al.*, "Direct Growth of Graphene Film on Germanium Substrate," *Sci. Rep.,* vol. 3, 08/19/online 2013.

[128] J.-H. Lee, E. K. Lee, W.-J. Joo, Y. Jang, B.-S. Kim, J. Y. Lim, *et al.*, "Wafer-Scale Growth of Single-Crystal Monolayer Graphene on Reusable Hydrogen-Terminated Germanium," *Science,* April 3, 2014 2014.

[129] K. S. Novoselov, V. I. Falko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, "A roadmap for graphene," *Nature,* vol. 490, pp. 192-200, 10/11/print 2012.