Growth of Millimeter-Sized Graphene Single Crystals on Al₂O₃(0001)/Pt(111) Template Wafers Using Chemical Vapor Deposition

Ken Verguts,^{1,2,*} Yves Defossez,^{1,2} Alessandra Leonhardt,^{1,2} Joke De Messemaeker,^{1,2} Koen Schouteden,³ Chris Van Haesendonck,³ Cedric Huyghebaert,^{1,2} Stefan De Gendt,^{1,2,**} and Steven Brems^{1,2,z}

¹Departement Chemie, KU Leuven, B-3001 Leuven, Flemish Brabant, Belgium

²Imec vzw, B-3001 Leuven, Flemish Brabant, Belgium

³Afdeling Vaste-Stoffysica en Magnetisme, KU Leuven, B-3001 Leuven, Flemish Brabant, Belgium

The synthesis of graphene using chemical vapor deposition on platinum surfaces is discussed. The crystalline nature of the platinum substrates as well as the graphene growth conditions play a key role to yield monolayer graphene with low defectivity. The need for template wafers with a single Pt orientation emerges due to graphene overgrowth on untextured polycrystalline Pt foils. Single-crystalline Pt foils can be obtained after long annealing steps. However, these Pt foils remain rough and are therefore less suitable during subsequent graphene transfer procedures. On the other hand, highly oriented platinum thin films avoid the overgrowth issues but result in differing nucleation phenomena on different oriented grains. An optimized graphene growth template is found in Al₂O₃(0001)/Pt(111), which is more than one order of magnitude flatter compared to the annealed Pt(111) foils and serves as an ideal catalyst to grow graphene grains exceeding 7 mm in diameter.

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Graphene has attracted a lot of research interest since its isolation by Geim and Novoselov in 2004.¹ A variety of graphene synthesis techniques evolved hereafter including top-down techniques as mechanical¹ and chemical exfoliation² or the reduction of graphene oxide.³ Also, bottom-up synthesis techniques such as epitaxial growth on SiC⁴ and chemical vapor deposition (CVD)⁵ on catalytic substrates are studied extensively. However, amongst these techniques only the CVD process has the ability to yield wafer-scale graphene at low cost with a relatively perfect structure and excellent properties. This CVD process often makes use of catalytic metal surfaces (e.g. copper,⁶ germanium,⁷ nickel,⁸ platinum⁹ and ruthenium¹⁰), heated in a carbon containing environment. Since every metal has its unique properties (e.g. carbon solubility, melting point, . . .), some candidates are more suitable for the growth of high-quality single-layer graphene (Ge, Cu and Pt). In this work, we explore platinum templates because defect-free monolayer graphene synthesis has been shown, with high mobility values after transfer to SiO₂ surfaces.¹¹ Platinum is of particular interest due to its oxidation resistance and the possibility to grow large single-crystalline graphene islands. It has been shown that defects can be healed and one can control the edges to be either zigzag, or armchair.¹² Furthermore, Pt foils were reused for more than 1,000 times. In addition, a lack of orbital hybridization between Pt and graphene results in a very weak chemical bonding,¹³ which is essential during the subsequent transfer process where graphene delamination is essential.^{14,15} Ion intercalation based graphene transfers were demonstrated.¹⁶

Graphene growth on Pt surfaces has been demonstrated to use two different mechanisms, which differ in the process step in which graphene is actually formed. The first mechanism relies on the cracking of hydrocarbons catalyzed by the Pt. Next, a graphene lattice is formed on the Pt surface. Net graphene growth occurs when the carbon deposition rate is higher than the carbon absorption rate into the bulk Pt.¹⁷ The second mechanism consists of the formation of multilayer islands, which occurs during the cooling phase. Dissolved carbon adatoms segregate to the Pt surface due to supersaturation caused by a decreasing temperature. This mechanism explains the presence

of multilayer areas, which are stacked in an inverted wedding-cake (IWC) configuration, with the graphene adlayer(s) sandwiched between the first graphene layer and the catalyst.^{18,19} This IWC configuration was also reported on other platinum group metals, as Ir(111)²⁰ and Ru(0001)²¹ as well as on copper foils.²² Back in 1991, Tontegode et al. studied the carbon adlayers on platinum on the basis of Auger electron spectroscopy results.²³ A minority of the adlayers are stacked in a wedding-cake configuration, as described by Wang et al.¹⁸ during an isothermal growth process. Recently, Wang et al.²⁴ reported another multilayer formation mechanism, found by performing in situ SEM measurements during graphene growth on Pt foils. The SEM shows clearly that graphene adlayers are formed at graphene grain boundaries and are formed when two non-aligned graphene islands merge together.²⁴

Also, on Pt surfaces, graphene-crystal edges are controlled and defects are removed by a growth-etch-regrowth procedure. However, oriented graphene growth on Pt(111) has not been observed.⁹ Solutions to minimize graphene grain boundaries can be achieved by synthesizing large (i.e. millimeter-sized¹⁶) graphene grains. Such processes require minimization of the nucleation center density and a following expansion of graphene domains by attachment of new C atoms to the existing graphene edges.¹⁶

In this work we perform a systematic study of graphene growth on Pt substrates. We start from polycrystalline Pt foils, which are subsequently annealed, resulting in an increased Pt grain size. Next, the growth of graphene on flat Pt thin films is studied. The selected Pt thin film candidate is Pt(111), which can be grown on scalable Al₂O₃(0001) wafers. The Pt(111) surface and the synthesized graphene sheets are presented in this paper. With this work we aim to contribute to the current state-of-the art by demonstrating the growth of millimeter sized graphene islands on scalable Pt template wafers.

Methods

Polycrystalline platinum foils (Alfa Aesar, 50 μm thick, 99.99% purity) are stable at high temperatures in a CH₄:H₂ ambient and were reused multiple times. In between every graphene growth run, the foils were cleaned thoroughly. This cleaning consists of several consecutive steps removing all carbon containing contaminants including polymers, photoresist and graphene from previous runs. First, the Pt

*Electrochemical Society Student Member.

**Electrochemical Society Fellow.

^zE-mail: Steven.Brems@imec.be

Figure 1. SEM image (a) and Raman spectrum (b) of graphene synthesized at a growth temperature of 600°C, for 20 min, using gas flows of 10:10:960 sccm ($\text{CH}_4:\text{H}_2:\text{Ar}$).

foil is immersed in acetone at room temperature for 20 min, rinsed in 2-propanol and dried using a N_2 gun. Remaining graphene fragments are removed by an oxygen plasma (10 min at 100 W) followed by a 10 min clean in a freshly prepared piranha solution (a 4:1 mixture of concentrated H_2SO_4 and H_2O_2). Lastly, the Pt foil is rinsed for 3 min in ultrapure water (UPW) and dried using a N_2 gun. It should be noted that the microstructure and crystallographic texture of the Pt foil changed over time. Due to grain growth, randomly oriented Pt grains were replaced by large, low surface energy (111) grains over time, due to the multiple high-temperature anneals in a reducing ambient.

Pre-cut and polished 2" Czochralski grown sapphire wafers (Roditi International Corporation) diced along the c-plane are used to prepare $\text{Al}_2\text{O}_3(0001)/\text{Pt}(111)$ template wafers. The monocrystalline wafers have a surface misorientation of $\leq 0.3^\circ$. The sapphire wafers were cleaned prior to Pt deposition in a 3:1 concentrated acid mixture of $\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4$ at 300°C for 20 min followed by a UPW rinse for 3 min.

Platinum deposition was performed by e-beam deposition in a Pfeiffer PLS 580 unit on a heated chuck, which was kept at approximately 550°C. The base pressure was 4×10^{-7} mbar after 12 h pumping using a turbo pump backed by a rotary pump. The platinum deposition rate was controlled by a quartz crystal rate monitor inside the deposition chamber and maintained to be about 1 Å s^{-1} . The platinum deposition was continued until a total thickness of 500 nm was reached.

Specific graphene growth conditions are described in the main text. However, all growth processes were performed in a vertical cold-walled Aixtron Black Magic 6" CVD system at a pressure of 750 mbar. The reactor is heated in a hydrogen atmosphere until the growth temperature is reached. Next, methane is introduced into the chamber. To end, the $\text{CH}_4:\text{H}_2$ gas flow ratio is decreased and the reactor is cooled down to room temperature at a cooling rate of $15^\circ\text{C min}^{-1}$.

Characterization of the substrates is done using scanning electron microscopy (SEM), atomic force microscopy (AFM), scanning tunneling microscopy (STM), electron backscatter diffraction (EBSD), X-ray diffraction (XRD) and X-ray reflectivity (XRR). Graphene is characterized using SEM, STM, Raman spectroscopy and low energy electron diffraction (LEED).

Graphene growth on polycrystalline platinum foils.—During the first step of the study, graphene synthesis on a polycrystalline platinum foil was explored. Figure 1a shows three different platinum orientations covered with mainly monolayer graphene, the darker contrast indicates the presence of multi-layered graphene regions. Growth was performed at non-optimized growth conditions by introducing gas flows of CH_4 , H_2 and Ar (resp. 10:10:960 sccm) for 20 min at 600°C.

The presence of several multilayer regions in the SEM image indicates many graphene nucleation sites, where the multilayer density and area depends on the platinum grain orientation. This observation is also reported by Wood et al.,²⁵ for graphene growth on polycrystalline copper substrates, and by Weatherup et al.,²⁶ who describe the areal coverage as a function of the growth time on different platinum grains. A higher multilayer graphene coverage is observed around platinum grain boundaries (see dashed line in Fig. 1a), suggesting a rapid carbon segregation from the bulk at these locations. Raman analysis after this low temperature graphene growth (see Fig. 1b) shows the presence of many sp^3 -hybridized carbon atoms, resulting in highly defective graphene as indicated by an I_D/I_G peak ratio of ~ 0.5 .

The microstructure of the platinum foil is explored using EBSD. Figures 2a–2b show an image quality and multicolored inverse pole figure (IPF) map of platinum grains with random orientation. The average grain size within one Pt foil is calculated to be $74 \mu\text{m}$ as seen on Figure 2c.

From the observation on polycrystalline platinum foils, we learn that there are three main challenges that will be difficult to overcome. First, the different graphene growth behavior on different Pt grain orientations. Second, the occurrence of carbon segregation at Pt grain boundaries and third, the formation of defective graphene. The first and second issue can be controlled using a single-crystalline metal template, avoiding platinum grain-dependence issues and thus resulting in a more uniform graphene growth behavior. The approach to solve the third challenge is to optimize the graphene growth conditions, such as to minimizing graphene grain boundaries (minimize graphene nucleation density) and obtain a lower I_D/I_G peak ratio (minimization of the amount of C sp^3 bonds).

To reduce the Raman I_D/I_G peak ratio, the graphene growth temperature is increased to 1050°C,²⁷ the growth time was extended to 1 h and the carrier gases were omitted. The H_2 flow is gradually decreased from 870 sccm to 820 sccm with steps of 10 sccm, while maintaining the CH_4 flow at 4 sccm. Therefore, the calculated CH_4 concentration increases from 0.458% to 0.485%. The corresponding SEM images, showing the graphene coverage as a function of carbon dose, are shown in Figure 3.

The uncovered area gradually decreases by decreasing the H_2 gas flow until the complete foil is covered with graphene, which is expected as H_2 promotes graphene etching.¹² The corresponding SEM images with carbon doses ranging from 0.458% till 0.480% are shown in Figures 3a–3e. At a carbon dose of 0.485% (see Fig. 3f), a full coverage of monolayer graphene is obtained and several multilayer spots can be observed.

Notably, the graphene nucleation behavior is dependent on the different platinum orientations, i.e. the incubation time differs from grain to grain. Therefore, graphene grain growth is observed on some platinum grains, while others remain uncovered.²⁶ With this we confirm that even with optimized growth conditions, the difference in

Figure 2. Image quality (IQ) (a) and IPF map (b) of an as-received polycrystalline platinum foil. The colors show the different grain orientations. The graph in (c) represents the grain size distribution, with an average grain size of 74 μm .

crystallization behavior dominates the graphene growth process. As such, the need for a single crystalline template is highlighted in order to obtain high-quality graphene with large grain size. In some cases, single graphene crystals can overgrow the platinum grain boundaries. In our experiments, this overgrowth can be observed for methane concentrations between 0.458% and 0.480% (see Figs. 3a–3e) and is likely also present, although not visible, in the fully closed graphene sheets (see Fig. 3f).

Additionally, the narrow window of growth conditions yielding graphene on platinum should be noticed. The first graphene layer is not closed in Figure 3e, which was grown with a carbon dose of 0.480%. However, when the carbon dose is increased slightly, to 0.485%, multilayer graphene areas start appearing, as seen in the inset of Figure 3f. To end, on polycrystalline Pt foils, no conditions were found yielding wafer-level scale single layer graphene coverage without any multilayer area. As the majority of multilayer graphene islands occur at Pt grain boundaries, it is clear that the development of a crystalline platinum template is beneficial for the improvement of CVD graphene growth on Pt surfaces. Therefore, we started to assess whether annealed Pt foils are feasible to reduce the amount of Pt grain boundaries and thus reduces the amount of nucleation sites.

Figure 3. Graphene synthesis on Pt foils. The CH_4 flow was set at 4 sccm and the H_2 flow ratio was varied from 870 sccm to 820 sccm with steps of 10 sccm. The corresponding carbon dose increases from 0.458% to 0.485% (a)–(f). The inset in (f) is a magnification of a graphene multilayer spot.

Graphene growth on annealed platinum foils.—Due to the challenges associated with polycrystalline Pt foils, the possibility of achieving crystalline Pt foil templates was explored, which offers the possibility of uniform nucleation density and wafer scale single layer graphene growth.

Pt(111) could be obtained by annealing Pt foils for long times in reducing ambient at low-pressure. Then, the polycrystalline platinum foils transform into the thermodynamically more stable (111) form. The (111) planes have the lowest surface energy in fcc crystals, providing a growth advantage to (111) oriented grains.²⁸ The preferred (111) orientation is revealed by the monochromatic color in the IPF map (see Figs. 4a–4b), whereas the full color spectrum was found in the IPF map of non-annealed platinum foils (see Fig. 2b), describing its polycrystalline nature. The intense signal in the inverse pole figure image also revealed a strong preference for the (111) orientation for annealed foils. The remaining small grains are (001) oriented, however the large curvature of high angle grain boundary between large (111) grains suggests that grain growth is still ongoing.

The difference in platinum grain sizes is also remarkable. The mean grain size for non-annealed platinum foils was 74 μm , whereas the mean grain size after annealing increases to beyond 2420 μm (tool limit). This grain growth suggests the possibility to completely transform polycrystalline platinum foils into Pt(111) foils.

While this result is promising, graphene grown on such crystalline substrates is not ideal for integration because of its high roughness. Although the Pt grain boundaries do disappear after annealing, the location of these grain boundaries can still be observed when measuring the topography of the Pt foils (see Fig. S1). The root mean square (rms) roughness on an annealed Pt foil is 11.55 nm (see Figs. 4c–4d), which complicates the following graphene transfer. For this reason

Figure 4. IQ (a) and IPF (b) map of an annealed polycrystalline platinum foil. The blue color in the IPF map reveals an almost complete transformation from a random texture to a single $\langle 111 \rangle$ fiber texture. (c) Non-contact AFM image and (d) corresponding height profile of an annealed Pt(111) foil.

we explore flatter crystalline Pt alternatives. In the next section, rigid crystalline Pt wafers are discussed.

Preparation of crystalline Pt(111) template wafers with twin boundaries.—As described in the previous section, Pt(111) is the preferred orientation for thermally driven grain growth. Therefore, we now focus on this orientation when exploring graphene growth on c-plane sapphire wafers. Growing on wafers offers the advantage of having a lower roughness compared to the Pt foils.

Choi et al.²⁹ demonstrated graphene growth on textured Pt(110) surfaces, which was deposited on Si/SiO₂ surfaces. Single crystalline Pt(110) can be obtained on Mg(110). However, Pt is susceptible to dewetting on MgO surfaces, which makes single crystalline Pt(110) thin films difficult to scale. A summary of Pt(110) template preparation and CVD graphene growth results on Pt(110) can be found in the supporting information.

To grow high-quality monolayer graphene, flat Pt(111) template wafers are developed. A 500 nm thick Pt layer was deposited on c-plane sapphire using physical vapor deposition.³⁰ By heating the sapphire substrate during Pt deposition, ordered Pt thin films with atomically flat terraces and monoatomic steps were obtained.³⁰ Platinum deposition at high temperatures is crucial for obtaining highly (111)-oriented Pt thin films with large Pt(111) grains.³¹ A high resolution XRD $\Theta/2\Theta$ measurement in Figure 5a shows the sapphire peaks, found at 41.7° for Al₂O₃(0006) and at 90.8° for Al₂O₃(00012), as well as the Pt(111) and Pt(222) peaks, which are found at 39.6° and 86.3° respectively. Other Pt orientations are absent. The azimuthal scan of the {111} planes shows a peak separation of 60° , indicating the presence of twin boundaries in the Pt(111) layer (see Fig. 5b). The XRR measurement is performed on an Al₂O₃(0001)/Pt(111) tem-

Figure 5. (a) The $\Theta/2\Theta$ XRD scan indicates a direct growth of Pt(111) (500nm) on a c-plane sapphire wafer. (b) The azimuthal XRD scan of the {111} planes shows a peak separation of 60° , indicating the presence of one orientation relationship (OR) with twinning. (c) Well-resolved Kiessig fringes suggest the very low surface roughness on a 20 nm thick Pt film. (d) Non-contact AFM image and (e) corresponding height profile of triangular Pt(111) terraces (500 nm thick Pt film).

plate wafers with a nominal Pt thickness of 20 nm. Figure 5c shows both the measured and fitted XRR curve of the Al₂O₃(0001)/Pt(111) (20 nm) sample. The well-resolved Kiessig fringes suggest that the interface in the thin films has sharp density gradient and extremely low surface roughness. The Pt thin film's surface roughness almost equals the sapphire's roughness (0.201 nm vs. 0.200 nm respectively). However, these 20 nm thin templates cannot be used as graphene growth templates, since the sapphire/Pt interface is not stable at these high graphene growth temperatures in a hydrogen containing environment.³² The Pt thickness was therefore increased to 500 nm to enhance the template stability. Large triangular Pt(111) terraces are also observed on these 500 nm thick films by non-contact AFM (see Fig. 5d). The step height in the line scan (see Fig. 5e) is about 0.23 nm, which corresponds to a single-atomic Pt step (0.238 nm).³³

CVD graphene growth on crystalline Al₂O₃(0001)/Pt(111) templates.—In order to minimize graphene grain boundaries, one can either grow oriented graphene to allow seamless stitching,³⁴ or minimize the amount of nucleation centers and grow the single-nuclei as large as possible. LEED measurements of graphene grown on a Pt(111) were performed by Cazzanelli et al.³⁵ Two possible orientations were found for graphene on Pt(111): R0 and a tilted R30 with a spread around the value. Since there is no single preferential orientation of graphene on Pt(111), we minimized graphene grain boundaries by aiming at a low nucleation density. This was achieved by tuning the CH₄ and H₂ partial pressures, which allows controlled graphene etching.^{36,37} The optimized parameters are found to be a gas mixture of 6:850 sccm CH₄:H₂, introduced into the reactor chamber at 750 mbar for 30 min. The growth temperature is varied from 1050°C to 1080°C by steps of 10°C (see Figs. 6a–6d), yielding graphene grains with

Figure 6. SEM images of graphene grown on $\text{Al}_2\text{O}_3(0001)/\text{Pt}(111)$ at respectively 1050 °C (a), 1060 °C (b), 1070 °C (c). Photograph of graphene on $\text{Al}_2\text{O}_3(0001)/\text{Pt}(111)$ grown at 1080 °C, graphene grains are visualized after spin coating with PMMA (d). Corresponding STM images of (d) measured at different magnitudes (e and f).

diameters up to 7 mm at 1080 °C. The orientation of the steps in the STM measurements (see Fig. 6e) reflects the symmetry of the Pt(111) surface. Zooming on a flat Pt terrace reveals graphene's atomic structure (see Fig. 6f).

Conclusions

Different Pt surfaces are studied and the importance of the crystalline orientation is highlighted. Furthermore, it is shown that the formation of monolayer graphene on Pt foils is not straightforward due to the narrow process window. A small change in H_2 concentration has a large effect on monolayer graphene coverage.

Synthesis on platinum foils is not preferred due to a specific nucleation behavior on different platinum grains, depending on grain orientation. Due to the nucleation behavior, the formation of the second monolayer occurs almost instantaneous with the closure of the first layer, such that growth conditions yielding 100% monolayer coverage were not found. However, extensive annealing revealed migration toward (mostly) single crystalline foils with a (111) orientation. Nevertheless, roughness of the Pt foils remains large, which is disadvantageous to developing a subsequent graphene transfer.

Studied optimization of growth templates and conditions leads to the growth of high-quality graphene on atomically flat $\text{Al}_2\text{O}_3(0001)/\text{Pt}(111)$ template wafers using a low methane to hydrogen gas flow ratio and high growth temperatures. Also here, the growth window to obtain monolayer graphene without the occurrence of multilayer areas is very narrow. The formation of graphene single crystals in the millimeter range is demonstrated.

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ORCID

Ken Verguts <https://orcid.org/0000-0001-7060-3024>
 Yves Defossez <https://orcid.org/0000-0002-2395-4056>
 Alessandra Leonhardt <https://orcid.org/0000-0002-1110-6949>
 Joke De Messemacker <https://orcid.org/0000-0002-4872-0176>
 Cedric Huyghebaert <https://orcid.org/0000-0001-6043-7130>
 Stefan De Gendt <https://orcid.org/0000-0003-3775-3578>
 Steven Brems <https://orcid.org/0000-0002-0282-8528>

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