Deposition of Nanocrystalline Multilayer Graphene Using Pulsed Laser Deposition

Yuxuan Wang , Bin Zou , Bruno Rente , Neil Alford , Peter K Petrov *

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Article

Deposition of Nanocrystalline Multilayer Graphene Using Pulsed Laser Deposition

Yuxuan Wang [1], Bin Zou [1], Bruno Rente [1], Neil Alford [1] and Peter K Petrov [1,*]

Imperial College London; yuxuan.wang18@imperial.ac.uk (Y.W.); b.zou@imperial.ac.uk (B.Z.); b.rente@imperial.ac.uk (B.R.); n.alford@imperial.ac.uk (N.A.); yux@imperial.ac.uk (P.K.P.)

* Correspondence: p.petrov@imperial.ac.uk

Abstract: The wide application of graphene in the industry requires the direct growth of graphene films on silicon substrates. In this study, we find a possible technique to meet the requirement above. Multilayer graphene thin films (MLG) are grown without a catalyst on Si/SiO_2 by pulsed laser deposition (PLD). It was found that the minimum number of laser pulses that are required to produce fully covered (uninterrupted) samples is 500. This number of laser pulses resulted in samples that contain ~5 layers of graphene. The number of layers was not affected by the laser fluence and the sample cooling rate after the deposition. However, the increase of the laser fluence from 0.9 J/cm^2 to 1.5 J/cm^2, results in 2.5 fold reduction of the MLG resistance. The present study reveals that the PLD method is suitable to produce nanocrystalline multilayer graphene with electrical conductivity of the same magnitude as commercial CVD graphene samples.

Keywords: graphene; pulsed laser deposition; nanocrystallization

1. Introduction

Since its discovery in 2004, graphene has gained more and more attention from various research areas. However, the wide application of single-layer graphene is still challenging due to the low efficiency of traditional mechanical exfoliation and the low grain size of graphene produced by CVD methods. Multilayer graphene attains a better trade-off between expense and physical property. Furthermore, unconventional superconductivity of bilayer graphene with magic angle has been discovered recently[1]. Thus, developing a quick and simple method to grow multilayer graphene on the desired substrate is essential.

Graphene is a new allotrope of carbon. Having been discovered by KS Novoselov and AK Geim[2] in 2004, graphene has attracted plenty of attention from various fields. Graphene is noted for its high carrier mobility[3], about 15000 $cm^{-2}V^{-1}s^{-1}$, high light transparency of 97%, the realization of room temperature quantum Hall effect[4], and high Young's modulus of 1TPa[5].

Although many different growth methods had been developed since the discovery of graphene, CVD and mechanical exfoliation are still the two most commonly used methods. However, the CVD method can only facilitate the growth of graphene on metal foil, which requires a further transfer process and can introduce contamination and additional cost. Mechanical exfoliation produces high-quality graphene thin film but has a sample size limitation and is very time-consuming.

Moreover, single-layer graphene is not required for many practical applications such as electrical conducting materials. A method that can directly grow multilayer graphene layers on the silicon substrates is required. As a widely used physical vapour deposition method, PLD has been used to grow ceramic thin films for several decades.

This paper explores the deposition process of multilayer graphene by the PLD method and presents the influence of laser fluence and the cooling rate after the deposition on the properties of the samples.

2. Materials and Methods

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PLD graphene growth: 1×1cm^2 Si/SiO_2 substrates with 9m0nm oxide layer were mounted on the substrate holder first, and then the substrate was heated to 800℃ at the rate of 50℃/min in the vacuum level of 3×10^{-5} Torr. Then 500 pulses of KrF laser (248nm) with the frequency of 10Hz ablated the graphite target for the graphene deposition. Once the deposition was finished, the samples were cooled at different rates to 305℃ after which natural cooling was applied to room temperature.

X-ray photoelectron spectroscopy (XPS) experiments and measurements were performed with Kα+ and an Al radiation source (hν = 1486.6 eV) in an ultrahigh vacuum chamber for spectroscopic analysis with a base pressure of 5 × 10^{-8} mbar

Raman spectroscopy measurements were performed using a LabRAM HR Evolution HORIBA Raman spectrometer with a laser wavelength of 532 nm (excitation energy EL = ħwL = 2.33 eV) which used an optical fibre, an objective lens of 100X, and NA = 0.8, resulting in a laser spot of 0.4 μm. The laser power was kept below 2 mW and the spectral resolution was ~3 cm^{-1}; the Raman peak position was calibrated based on the Si peak position at 520.7 cm^{-1}.

Asylum Research MFP-3D AFM system was used to characterize the topology of graphene samples and the thickness of the multilayer graphene.

16 Au(50nm)/Ti(5nm) electrodes with the diameter of 1mm were deposited on the surface of the graphene samples by magnetron sputtering. The resistance across the graphene samples were measured using a probe station (Model: Signatone S-1160) and a Keysight B1500 Semiconductor Analyzer

3. Results

The Raman spectra of multilayer graphene grown on Si/SiO2 substrate using the PLD method with laser fluences of 0.9 J/cm2 and 1.5 J/cm2 are shown in Figure 1. The deposition was carried out in vacuum condition (3×10-5 mTorr) at a temperature of 800℃, and then the sample was cooled down to room temperature at a rate of 50℃/min. In both Raman spectra, the D peak is higher than the G peak and the 2D peak is highly broadened with lower intensity compared to the G peak. According to Wu Jiang-Bin et al.[6], this indicates that the obtained graphene is polycrystalline with nano-sized grain. This also explains the broad 2D peak and high D peak since a large number of grain boundaries increases the graphene defect density.

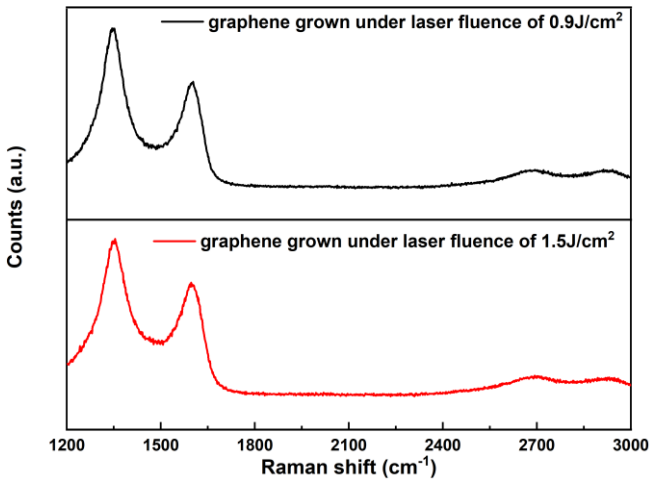

Figure 1. The Raman spectrum of multilayer graphene grown on Si/SiO2 substrates with the PLD method at the cooling rate of 50℃/min under 0.9 and 1.5J/cm2 respectively. The Raman spectrum confirms that the thin film grown with the PLD method is nanocrystalline graphene with multilayers. The graphene obtained under different laser fluences produces similar Raman results indicating that the intrinsic of graphene doesn't change at least in the range of laser fluence from 0.9-1.5J/cm2.

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X-ray photoelectron spectroscopy was used to further characterize the samples. The result is shown in Figure 2 from which C1s, O1s, and Si2p are characterised. The C1s peak can be seen as the sum of the sp2 carbon, C-O, C=O, and C-H. In both samples, the sp2 carbon takes the highest portion which means that both samples are graphene. However, the proportion of signal from other types of carbon atoms in graphene grown with a laser fluence of 0.9J/cm2 is higher than that in graphene grown with 1.5J/cm2. This means that the quality of graphene improves with the increase of laser fluence. Also, the portion of C-O in the O1s signal from the graphene sample grown with 0.9J/cm2 fluence is also higher than the one grown with 1.5J/cm2. This further confirms the drawn conclusion.

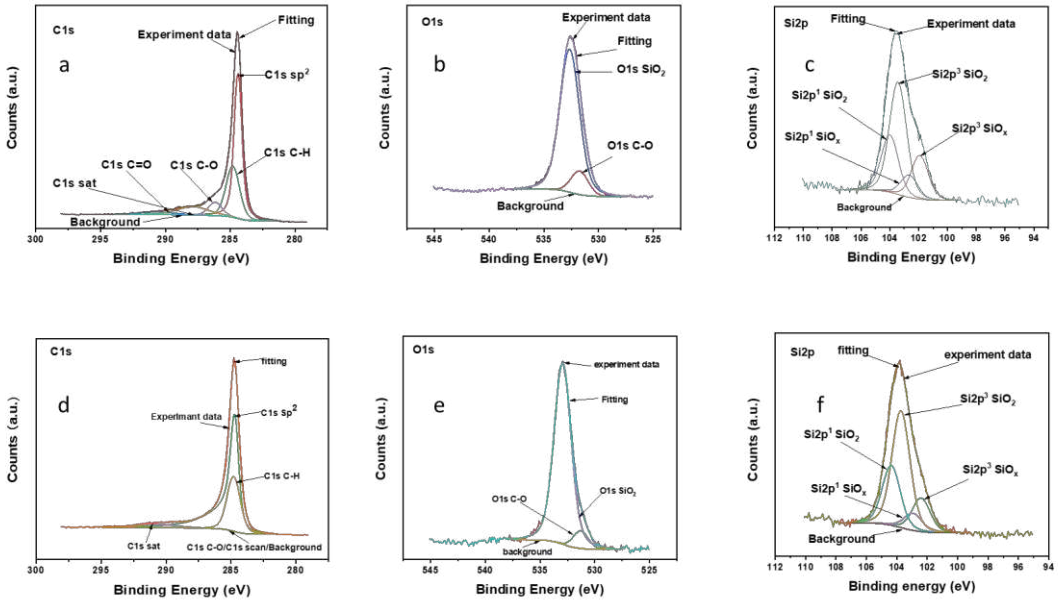

Figure 2. The XPS result of the graphene sample grown at the cooling rate of 50°C/min under 0.9J/cm2 (a,b,c) and 1.5J/cm2 (d,e,f). The C1s, O1s, and Si2p of these two samples are shown above. The C1s result of both samples shows that most carbon atoms in the samples are sp2 hybridized which indicates that the sample obtained is graphene. The proportion of the sp2 carbon signal in the total carbon signal and the portion of the C-O oxygen signal in the total oxygen signal also shows that the quality of the graphene grown under 1.5J/cm2 is better than the quality of graphene produced under 0.9J/cm2.

To explore the effect of the cooling rate on the quality of graphene, multilayer graphene samples, after the deposition, were cooled down at a rate of 5, 10, 20, 30, 70, and 90°C/min. The laser fluence was kept at 0.9J/cm². It was observed that the Raman spectra are very similar, and not affected by the cooling rates. This means that the polycrystal intrinsic nature of the graphene sample is not influenced by the cooling rate.

Another parameter that can affect the quality of graphene is its number of layers. Traditionally, only carbon thin films with a number of layers in the range of 5-10 can be seen as multilayer graphene while graphene with a number of layers less than 5 can be called few-layer graphene. The number of layers could be evaluated using equation (1) derived by Bayle, Maxime et al.[7].

$$N_G = 1.05 \times A_G^{norm} + 0.16 \times (A_G^{norm})^2 \quad (1)$$

where A_G^{norm} is the ratio between the G peak area of the graphene sample and the G peak area of the graphite target.

The number of graphene layers evaluated for all samples are presented in Figure 3. It is around 5 and is not affected by either laser beam fluence or sample cooling rate. This shows that the difference in graphene quality is not aroused from the number of layers.

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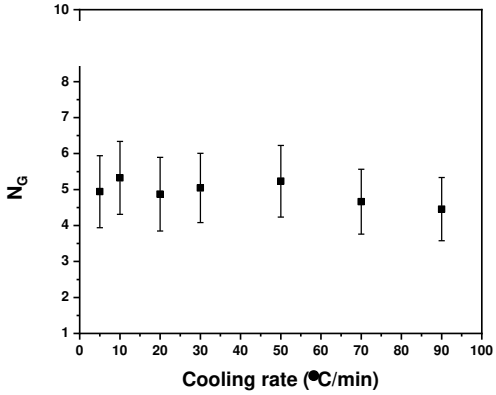

Figure 3. The calculated number of layers of graphene grown under different cooling rates. The number of layers of these graphene samples is all around 5 and not affected by laser fluence.

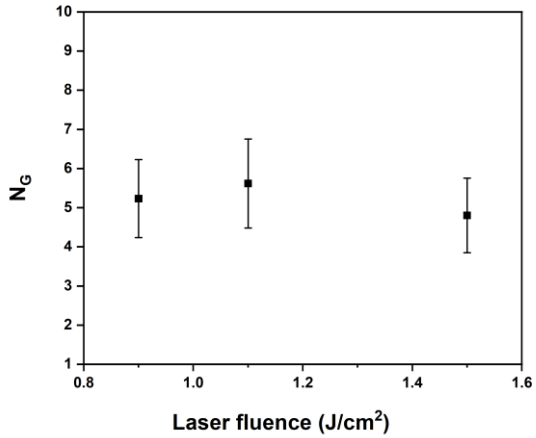

Figure 4. The number of layers of graphene grown under different laser energy. An additional sample is fabricated under the laser fluence of 1.1J/cm^2 at the same cooling rate. The deposition energy does not affect the number of layers.

The verification of the above estimation was done by characterisation using AFM of the edges of graphene samples grown with a laser fluence of 0.9J/cm2 and a cooling rate of 50°C/min. The typical AFM image is shown in Figure 5. The average thickness of this graphene sample is around 1.5-2nm. Since the thickness of single-layer graphene is 0.335nm, the number of layers of the graphene sample is about 5-6.

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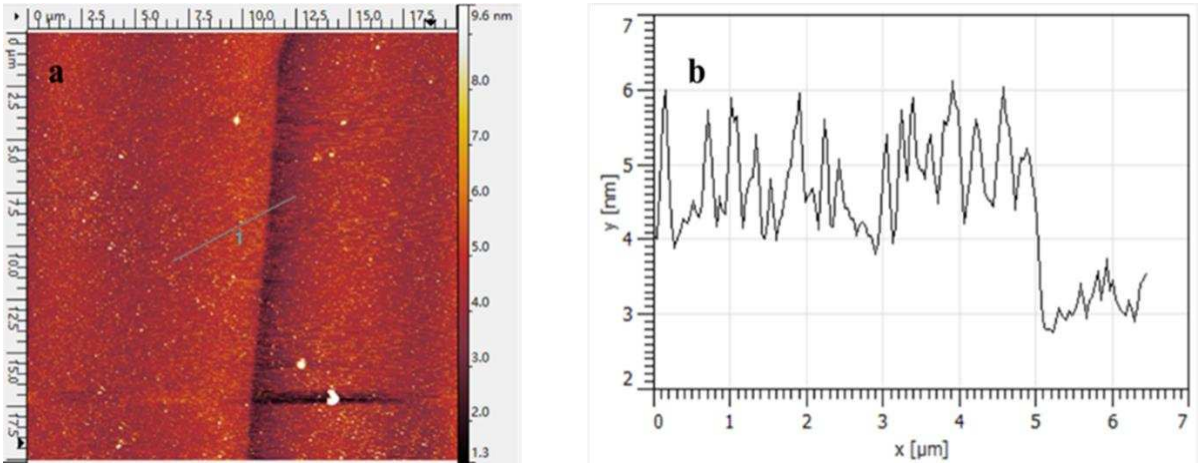

Figure 5. The AFM image of the graphene sample grown under 0.9J/cm² at the cooling rate of 50°C/min (a). The profile was plotted across image (b). The profile shows that the thickness of the graphene sample is about 1.5-2nm which corresponds to 5-6 layers.

To evaluate the quality of the graphene sample, the electrical resistance of the graphene samples was measured four probe measurement methods. The result is shown in Figure 6. Evidently, the resistance of graphene samples is affected by laser fluence. By fixing the cooling rate at 50°C/min, the resistance of graphene was ~15kΩ for the samples ablated with a 0.9J/cm2 laser energy and ~6.6kΩ when the laser energy was 1.5J/cm2. This result confirms the conclusion based on the XPS result that graphene grown with laser fluency of 1.5J/cm2 has better quality.

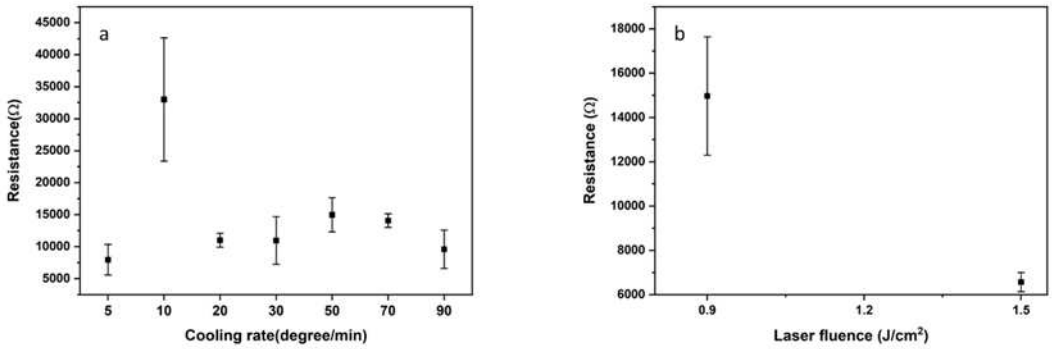

Figure 6. The resistance of graphene grown under laser fluence of 0.9J/cm² at a different cooling rate (a). The resistance of graphene grown under different laser energy at the cooling rate of 50°C/min (b). The resistance of graphene grown under 0.9J/cm² is almost three times that of graphene grown under 1.5J/cm² while the resistance of graphene grown under laser energy of 0.9J/cm² is in the range of 10-30kΩ.

With a reference to Figure 6, among all graphene samples grown with a laser fluence of 0.9J/cm² and various cooling rates, the sample cooled down at a rate of 10°C/min shows the highest resistance. This is a surprising result and lacks explanation. A possible explanation could be that 10°C/min is a critical cooling rate that will affect the crystallisation of carbon atoms during the formation of graphene thin films.

All samples are nanocrystalline multilayer graphene and their resistance depends on the grain size and affects the FWHM of the G peak of the samples' Raman spectrum[8]. The FWHM of all graphene samples is presented in Figure 7. Comparing the change of FWHM with the cooling rate, laser energy and the change of resistance, it can be concluded that the resistance and FWHM of the G peak are inversely proportional. This contrasts with the results observed for graphene monolayer samples, where the broadening of the G peak is associated with the smaller grain size and leads to

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increased resistance. This unusual behaviour can be attributed to the multilayer origin of the graphene samples.

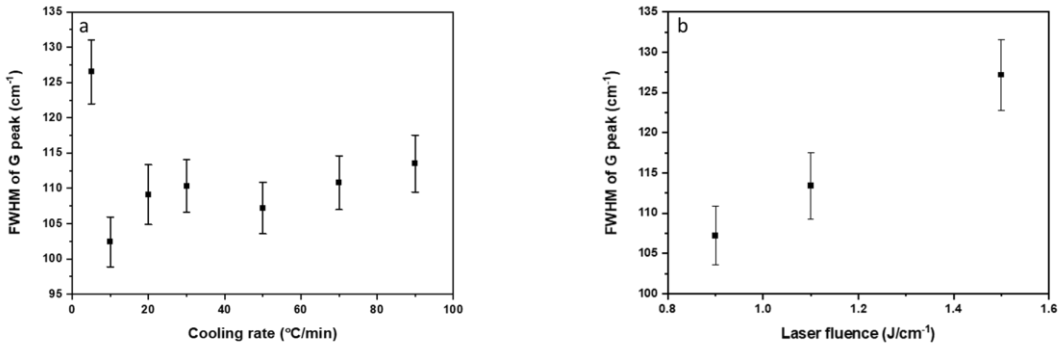

Figure 7. The FWHM of graphene samples grown under 0.9J/cm2 at different cooling rates (a) and graphene samples grown at the cooling rate of 50°C/min under different laser fluence (b). The trend of the FWHM change of graphene samples is exactly opposite to that of the resistance of the same graphene sample.

To evaluate the relationship between the FWHM of the G peak and the resistance of multilayer graphene samples, their values were plotted (see Figure 8). The equation of the fitting curve representing the experimental results is shown in equation (2).

$$\mathbf{R(\Omega)}=\boldsymbol{R_0}+\mathbf{A}\exp(-(\boldsymbol{\Gamma_G}(\boldsymbol{cm^{-1}})-\boldsymbol{\Gamma_{G0}})/\boldsymbol{t}) \quad (2)$$

where $\boldsymbol{R_0}$=7.7±1.1kΩ, $\boldsymbol{\Gamma_{G0}}$=102.5cm^{-1}, A=25492.3, t=3.4±0.6cm^{-1}. Detailed statistical analysis requires further investigation and more experimental data.

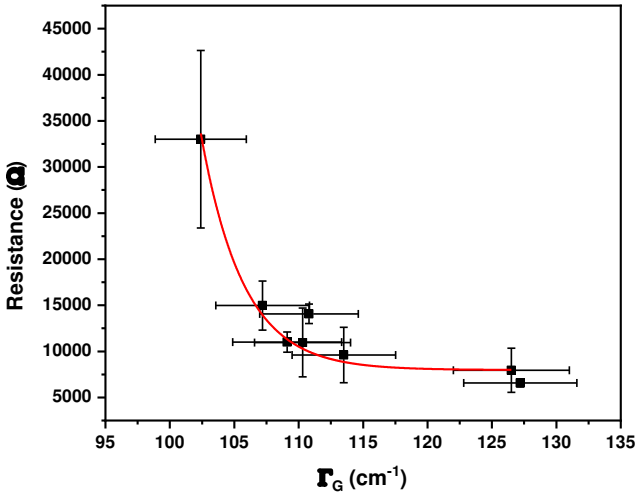

Figure 8. The plot between FWHM of G peak and electrical resistance of graphene samples grown under different laser energy and cooling rate. A fitting curve can be plotted to estimate the resistance of the graphene sample with a certain FWHM.

4. Discussion

The present study reveals that the PLD method is suitable to produce nanocrystalline multilayer graphene. It was found that the minimum number of laser pulses that are required to produce fully covered (uninterrupted) samples is 500. This corresponds well with studies reported elsewhere (e.g., S.C Xu et al.[9]). This number of laser pulses resulted in samples that contain ~5 layers of graphene.

This result was confirmed by both Raman and AFM measurements. The number of layers was not affected by the laser fluence and the sample cooling rate after the deposition.

Based on the electrical measurements, it can be concluded that the electrical resistance of graphene samples is mainly affected by the laser fluence during the depositions and it is almost independent of the cooling rate after the deposition. The resistance of graphene samples decreases from 15kΩ to 6.6kΩ when the laser fluence increase from 0.9J/cm^2 to 1.5J/cm^2. This suggests that the resistance of graphene could be further reduced by increasing the laser fluence, however, Xu et al. report, the quality of graphene deteriorates when the laser fluence is higher than 6J/cm^2.

Usually, a decrease in the grain size of graphene is manifested by the increase of the FWHM of the G peak of the Raman spectrum. In our case, this relationship does not hold (see Figure 8). A possible explanation for this could be that the grain size is not the only factor contributing to the resistance of the multilayer graphene grown with the PLD method.

Author Contributions: Y.W. and P.K.P. conceived and designed the research. Y.W, B.Z and B.R carried out the experiments. All authors contributed to the paper discussions and manuscript drafting. All authors have approved the final version of the manuscript**.**

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Data Availability Statement: The datasets generated during and/or analysed during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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