Control of Graphene Layer Thickness Grown on Plasma Enhanced Atomic Layer Deposition of Molybdenum Carbide

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Abstract

Multilayer graphene (MLG) films grown on molybdenum carbide (MoC\textsubscript{x}) substrates. We fabricated the catalytic MoC\textsubscript{x} films by plasma enhanced atomic layer deposition (PEALD) and grown the MLG by low pressure chemical vapour deposition (CVD). We show the merits of ALD catalytic substrate for CVD graphene growth with high quality MLG on large area, excellent uniformity and layer homogeneity. Moreover, we demonstrate how to achieve control of graphene layers thickness and properties, by varying the specific catalytic film chemical and physical properties. The control of growth is not digital, but is broad ranged from few layer graphene to a graphitic film of \(\sim 75\) graphene layers grown on the respective ALD catalytic substrates. Characterisation of the MLG has been performed using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), spectral ellipsometry (SE), and scanning low-energy electron microscopy (SLEEM). By varying MLG thickness in a uniform homogeneous way, we can tailor the desired MLG properties for different application needs. Furthermore, the PEALD process can be readily adapted to high volume manufacturing processes, and combined with existing production lines.

1 Introduction

Graphene, a two dimensional sheet of carbon atoms, has attracted great interest in research because of its unique properties. A vast field of applications could utilise graphene to realise the next generation technology \[1,2\]. Consequently, the ability to fabricate this material in a uniform scalable method and integrate into applications is the main challenge for both industry and academia. Various techniques have been explored to prepare graphene sheets, such as liquid phase exfoliation \[3\], epitaxy on SiC \[4\] and chemical vapour deposition (CVD) \[5\]. Among these, CVD is the most promising for industrial scale production of high
quality graphene. Graphene can be grown by CVD on a variety of catalytic metallic substrates, including Cu, Co, Ni to name a few. CVD growth on Cu allows for growth of mostly single layer graphene sheets, but Cu grain size induce a polycrystalline graphene growth with defects on the graphene grain boundaries. Cu foils are commonly used for growth, and graphene defects form along the Cu railing sites. Sputtered Cu thin film can mitigate Cu foil related defects, but the thin film has its limitations as well [6, 7]. Graphene growth is performed close to the melting point of Cu causing mass loss of Cu and subsequently holes in the film due to dewetting. The difference between the thermal expansion in the Cu itself and the substrate cause for strain which leads to a wrinkly graphene sheet. Ni is commonly used for growth of multi-layer graphene (MLG), due to the high solubility of carbon in Ni. While MLG grown on Ni is typically not uniform due to island like growth around the Ni grain boundaries, significant advancements have been made [8, 9]. Recently, a scalable and uniform growth of MLG has been demonstrated on Mo thin films deposited by physical vapour deposition (PVD) [10, 11]. Mo has the advantage of a higher melting point than Cu, which vital to reduce mass loss during growth. Furthermore, a similar thermal expansion coefficient to Si (4.8 and 2.6 μm·m⁻¹·K⁻¹) as oppose to Cu (17 μm·m⁻¹·K⁻¹), that reduces stress during growth and thus wrinkles in the graphene layers. Mo has also the advantage of being a clean room compatible material commonly used in IC manufacturing environment. However, PVD Mo thin films still suffer from limitations related to the deposition technique. For the next generation applications, requirements for film uniformity, coverage and homogeneity are very strict, and PVD has reached its limitations in a high aspect ratio (HAR) topologies. As PVD utilises highly kinetic ion bombardment to deposit the film, it is not suitable for coating MLG if a stack layer is required, as it will severely damage the MLG. Finally, impurities in sputtered Mo will also contribute to defects in the grown MLG. We present here a demonstration of MLG grown on molybdenum carbide (MoCx) substrate that we fabricated by plasma enhanced atomic layer deposition (PE-ALD) [12]. We refer to these samples as ALD MoCx films. Atomic layer deposition (ALD) allows for sub nanometre thickness control suitable for the strictest application demands to date. Additionally, we are able to tune the film composition and properties with high accuracy and reproducibility. Thus, high quality MLG is grown on large area, with excellent uniformity and homogeneity in CVD graphene fabrication. The technique is scalable to large volume manufacturing and is compatible with IC and sensors fabrication environment. In the characterisation section we compare graphene grown on various types of MoCx films. An overview of results is presented, depicting the characterisation and a comparison of the grown MLG.

2 Experimental methods

MoCx thin films have been deposited by plasma enhanced atomic layer deposition (PEALD) at various temperatures and plasma conditions. PEALD was
performed on 100 mm Si (100) wafers coated with 450 nm of thermally grown SiO$_2$. The depositions were performed in an Oxford instruments FlexAL2 ALD reactor, which is equipped with an inductively coupled remote RF plasma (ICP) source (13.56 MHz) with alumina dielectric tube. MoC$_x$ thin films have been deposited by PEAALD at various temperatures and plasma conditions, with MoC$_x$ films varying from 15µm to 30µm in thickness. MLG was grown by low-pressure CVD (LPCVD) in a quartz tube ($d$=50mm, $l$=60cm) furnace with 3 heat zones set to 1050°C. The typical base pressure when evacuated is 10$^{-3}$ mbar. The furnace is set on cart wheels, to allow samples to be rapid annealed, as furnace temperature stabilises within 3.5 minutes after tube insertion. When moved away from the furnace, sample cooling down duration is typically 15 minutes. Carbon feedstock gas ($CH_4$) is fed along with Argon through a quartz inner tube of 5 mm in diameter to the sealed side of the outer tube. Graphene films have been grown using CVD with $CH_4$/Ar gas flow at 1100°C.

3 Characterisation of Graphene Films

We studied the CVD grown MLG films, comparing graphene quality, uniformity and homogeneity. Characterisation of the MLG has been performed using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), spectral ellipsometry (SE) and scanning low-energy electron microscopy (SLEEM). The thermal stability of MoC$_x$ ALD film was very high, and no delamination or mass loss was noticed for all measured film thicknesses. The experiments presented here have been performed on ~ 25µm thick MoC$_x$ films. A comparative analysis has been performed in order to understand the correlation between the catalytic substrate properties and the subsequent graphene layers grown on top. Using PE-ALD MoC$_x$, we are able to control the characteristics MoC$_x$ film with excellent uniformity, by altering the MoC$_x$ film mass density and crystallinity as demonstrated in [12].

3.1 Raman Spectroscopy

Raman spectroscopy is a non-intrusive measurement which indicates graphene quality by the characteristic bands of graphene at 1350 cm$^{-1}$ (D peak) 1580 cm$^{-1}$ (G peak) and 2700 cm$^{-1}$ (2D peak). In short, the D peak is related to disorder in the graphene lattice and considered to indicate defects in the graphene layers. The ratio between 2D and G peak indicate the nature of the graphene, with MLG ranges between 0.4-0.8 2D/G ratio, while single layer graphene (SLG) ratio is typically > 1. The FWHM for SLG is 30cm$^{-1}$ and for MLG ranges between 60 - 120 cm$^{-1}$. Raman mapping scans were also used to characterise a large area by scanning multiple adjacent spots. We have analysed graphene samples on a large scale with non-intrusive methods, to gain statistical data on uniformity, homogeneity and defects of our graphene samples. To the best of our knowledge, this is the first time graphene quality has been quantified statistically by analysing single point Raman diagnostics.
of characteristic graphene spectra to produce an overview of the entire scanned sheet attributes. We measured areas of 30x30 µm² with 1 µm steps (laser spot resolution limit), to derive information on the MLG uniformity and defects variations. To do so, the 2D/G and D/G ratios were calculated from ~1000 scans for each area, for statistical analysis. Variations in 2D/G are a good indicator for uniformity of MLG layers. Both variation and value of D/G ratios are an indicator to amount of defects and uniformity in MLG layers. We show the results both in form of colour maps to visualise uniformity variations and as density distribution functions, to quantify these variations. The covariance of each dataset indicates the uniformity and homogeneity of the graphene layers. As seen in figure 1b the uniformity of MLG grown on MoCₓ ALD at 350⁰C is high, with typical ratio of MLG as well as FWHM of 2D peak. The narrow distribution function shows high MLG uniformity with 2D/G ratio at about 0.9 and variance of 1.5 · 10⁻². Similarly, MLG grown on MoCₓ ALD film fabricated at low deposition temperature exhibits high uniformity and low defects ratio [see table 1]. As can be seen in figure 1c, MLG grown on ALD film show lower average D/G peak ratios, indicating the overall high quality and uniformity, as confirmed by the low D/G covariance.

3.2 X-ray photoelectron spectroscopy

The film composition was analysed by X-ray photoelectron spectroscopy (XPS) with a Thermo Scientific KAI066 spectrometer, using monochromatic Al K x-rays with an energy of 1486.6 eV. The films were sputtered with Ar⁺ ion gun prior to scans, in order to remove surface oxide and adventitious carbon. A continuous electron flood gun was employed during measurements to compensate for charging. XPS is surface-sensitive quantitative spectroscopic technique, that allows for analysis of a substrate surface chemical composition. We compare MLG grown on various types of MoCₓ films with C1s core level spectra and reference it to graphene grown on Cu thin film. MLG grown on ALD films of type A shows pure carbon presence at the surface (within error margins) and no trace of the catalytic substrate or oxygen. The peak position confirms a sp² carbon bonds of MLG. As can be shown in figure 3b, the MLG has high purity sp² bonding with main contributing peak located at 284.4 eV. Due to the interaction of the photoelectron with free electrons in the film, a corresponding plasmon loss feature is observed at ~ 290.4eV signifying the graphene sheet conductivity. We can further examine the bulk of the material by etching with Ar⁺ ion gun to perform depth profiling and analyse the elemental composition and the nature of the chemical bondings of each layer. A comparison of MLG grown on various types of MoCₓ ALD films is performed by etching 100 levels (2000 seconds). As can be shown in figure 4 the MLG varies in thickness between different type of catalytic substrates, as indicated by diminishing C1s peak intensities [12]. The diminished peak intensities are accompanied with the rise of Mo peak, which indicates a transition to the underlying catalytic substrate. The thinnest graphene sample was measured on type C MoCₓ, with only 1 level with typical sp² carbon peak and ~ 65 at.% carbon on the surface, match-
ing typical values measured for graphene grown on Cu thin film. The thickest MLG layers have shown a consistent $sp^2$ carbon peak for all 100 etched levels, with no indication of any other element peak. Carbon content remained stable around $\sim 98\, \text{at.}\%$ as is shown in figure 4a.

3.3 Film Thickness Characterisation

3.3.1 ultra-low energy SEM/STEM of graphene

The electron transmissivity at low energy (up to tens of eV) has proven a reliable tool for counting graphene layers as an alternative to Raman spectroscopy, providing an enhanced lateral resolution. Graphene layers exhibit contrasts connected with electron reflectivity fluctuations below 8 eV and in an additional band around 15 eV in the ultra-low-energy SEM. This phenomenon can also be employed for counting the graphene layers with a correlation of n-1 minima reflectivity for n graphene layers. Studies of graphene layers number and homogeneity were performed, as shown in figure 5a, showing simulation of the fluctuations as a function of graphene layers as was simulated in VASP. Figure 5b shows measured fluctuations on ALD $MoC_x$ MLG sample corresponding to 6 layers of graphene (5 minima). Measurements performed concluded high layer homogeneity across the sample.

3.3.2 Spectral ellipsometry

Film thickness and optical properties of the deposited films have been studied with a J.A. Woollam UV-spectroscopic ellipsometer (SE). Data was obtained within the range of 190 nm–990 nm, and refractive index (n) and extinction coefficient (k) were determined. Figure 7 shows an extract of the layers thickness and composition, as modelled in CompleteEASE software. Relevant selected oscillators were chosen to achieve optimal fitting of the data ($MoC_x$ paper).

For a type A $MoC_x$ sample of $25 \pm 1\, \text{nm}$ thick film, we estimated an equivalent $25 \pm 1\, \text{nm}$ thick MLG film grown on top. The MLG thickness corresponds to approximately 75 graphene layers, as was confirmed with XPS depth profiling matching all etch levels to $sp^2$ carbon peak positions.

4 Discussion and Conclusions

We have demonstrated the effects of the catalytic substrate physical and chemical properties on the CVD grown MLG properties.

With the ability to precisely control PEALD $MoC_x$ composition, we can control the grown MLG film ontop. $MoC_x$ film with low density, low crystallinity and high carbon content (type A) are readily able to saturate and precipitate free carbon content required to form $sp^2$ carbon bonds on the surface, as oppose to crystalline $MoC_x$ films with high mass density (type D). Moreover, these $MoC_x$ films will yield MLG with significantly lower defects. $MoC_x$ mass density has shown to have a reverse proportion to MLG thickness, and a good
correlation to defects ratio in MLG film, as Type C films have shown to inhibit graphene growth.

The high crystalline type D film has shown to have high 2D/G ratio typical to FLG and a higher D/G ratio. The defects are likely occurring as the $\text{MoC}_x$ film transition from a cubic $\text{MoC}_{0.75}$ phase to orthorhombic phase during the high temperature MLG growth process [unpublished work].

The results presented have been collected over a time span of 18 months, with excellent reproducibility. While ALD reactor conditions may vary, the correlation between the ALD film and the CVD grown graphene remained identical.

Type A films with the lowest mass density and highest C/Mo ratio have produced the thickest MLG layers. A film of $\sim 25$ nm $\text{MoC}_x$ produced over 75 graphene layers, as was estimated by UV-SE. Type C high density film with low C/Mo ratio yielded the lowest number of MLG layers. We could accurately determine 6 graphene layers using SLEEM measurements grown on ALD $\text{MoC}_x$. Nevertheless, we stipulate thinner FLG could be achieved, as the Raman spectrum of type D graphene suggests. More work needs to be done in fine tuning MLG thickness, and more parameters should be looked at, specifically substrate thickness and crystallinity. In addition, other catalytic substrates should be evaluated, both as homogenous elements and alloys, for suitability [4].

By profiling the chemical composition of 100 etch levels, we could confirm our stipulation of MLG thickness control, with proportional increase in graphene film thickness to initial $\text{MoC}_x$ film C/Mo ratio and inverse to mass density. This control can be achieved very accurately using PEALD film, which allows for reproducible and scalable fabrication. Furthermore, the catalytic substrate purity, homogeneity and uniformity plays an important role to the same properties of the graphene grown on top, namely MLG defects, homogeneity and uniformity.

Therefore, a uniform homogeneous film is vital in order to optimise MLG quality. In this regard, ALD catalytic substrates would have an advantage over other commercial deposition techniques to achieve an overall higher quality film. In addition, the outstanding step coverage makes ALD a tool of choice if 3D objects are of interest.

By varying MLG thickness in a uniform homogeneous way, we can tailor the desired MLG properties for different application needs. Furthermore, the process is reproducible, and suitable for implementation in IC and sensors fabrication environments. The PEALD process can be readily adapted to high volume manufacturing processes, and combined with existing production lines.

The MLG film grown on $\text{MoC}_x$ ALD film demonstrated here is superior in quality and uniformity to other commercial CVD graphene fabrication techniques known thus far [unpublished work]. The rapid advancement in ALD tools and techniques such as role to role, batch production, and selective area PEALD promise a leap forward in advancing commercial high quality graphene production. By utilising recent developments in ALD, the path to next generation electronics based on high quality graphene is opened.
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5 Figures
| Temp.(°C)  | [C] (at%) | [O] (at%) | [Mo] (at%) | 2D/G | 2D/G variance | D/G | D/G variance |
|------------|-----------|-----------|------------|------|---------------|-----|-------------|
| High temp. | 97.9      | < d.l.    | < d.l.     | 0.96 | 1.5 · 10⁻²    | 0.19| 7 · 10⁻⁴    |
| Low temp.  | 98.5      | < d.l.    | < d.l.     | 0.91 | 2 · 10⁻²      | 0.31| 1.2 · 10⁻³  |

Table 1: MLG grown on type A MoCx. Atomic % of elements by XPS and summary of Raman scanning maps covariance values of the respective 2D/G and D/G peaks. A smaller covariance value corresponds to a higher uniformity MLG film.

Figure 1: Raman spectra of MLG grown on 25 µm thick MoCx ALD film. (a) Top: single Raman scan of the graphene. Bottom: Raman spectra of peaks ratio measured by a mapping scan of 30 × 30µm² area with 1µm step resolution. (b) Left: 2D/G peak ratio of MLG film. Variation in colour is inversely proportional to MLG uniformity. (c) Right: D/G peak ratio of MLG shows low D/G peak ratio with high uniformity.
Figure 2: Distribution function of MLG Raman peak ratios, based on \(\sim 1000\) scanning points per function. Narrower distribution is generally attributed to higher uniformity of MLG. A narrower distribution of the 2D/G ratio indicates higher homogeneity of the MLG.

Figure 3: XPS spectra of C1s core level. (a) Left: XPS C 1s spectrum of single layer graphene (SLG) on Cu PVD thin film. (b) Right: C1s scan of MLG on ALD MoC\(_x\). A typical asymmetric \(sp^2\) peak at 284.4 eV indicate high purity graphene material. Plasmon loss features at \(\sim 290.5\) and \(\sim 293\) are caused by interaction of the photoelectron with free electrons present in the graphene sheet. No sign of carbidic metal from catalytic substrate.
Figure 4: XPS depth profiling of MLG on ALD catalytic substrate. (a) High purity $sp^2$ carbon content is shown in top figure for the entire 100 etch levels (20s etch time) for MLG grown on type A substrate. No impurities are measured within the XPS error range ($\pm 2\text{ at.\%}$). (b) C 1s spectra of samples deposited at various conditions, demonstrating the control of MLG layer thickness. Type C substrate inhibits MLG growth, with merely 65% surface $sp^2$ carbon content, typical to $\leq 1$ graphene layer.
(a) DFT simulations of electron reflectivity fluctuations as function of number of graphene layers

(b) Lower energy bands

(c) Higher energy bands

Figure 5: Count of graphene layers by scanning low energy electron microscopy. Measurements of electron reflectivity in MLG/MoC\textsubscript{x} ALD sample at two energy bands. Simulations and measurements performed by Eliska Mikmekova (The Czech Academy of Sciences)
Figure 6: Overview of ALD $MoC_x$ temperature of deposition effects on graphene growth and properties. The effects of $MoC_x$ film on MLG are presented by comparison of D/G peaks as measurement with Raman mapping, % of graphene as determined by $sp^2$ peak positions in each etch layer, and % of carbon at the surface of the MLG that relates to the $sp^2$ peak position.