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Growth of multi-layered graphene on molybdenum catalyst by solid phase reaction with amorphous carbon

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Introduction

Since the discovery of graphene, several approaches to produce high quality material have been explored. Currently, the best techniques for industrial scale production are liquid phase exfoliation, epitaxial growth on SiC, electrochemical methods and chemical vapor deposition (CVD) [1–5]. CVD represents the most inexpensive and promising route suitable to combine high quality and purity graphene with large scale production, especially relevant for applications within semiconductor technology [6, 7].

In the conventional CVD process, graphene growth requires carbon supersaturation at the catalyst interface, usually at around 1000 °C [8]. Typical catalyst materials are transition metals, such as Cu, Co, Ni, Pt, Pd [9]. Among the possible catalysts, Cu is proved to be the best candidate for uniform single layer of graphene growth. Integration in a wafers based process, however, suffers from several disadvantages making Cu not the optimal catalyst choice. The low melting point causes deformation of the Cu thin film, while the thermal expansion coefficient mismatch with the silicon wafers creates large stresses and can induce roughness. Finally, Cu is an undesired element in most active devices. For few or multi-layered graphene (MLG), Ni is often used as a catalyst. Nickel is however known to result in graphene layers with a large thickness variation at the microscale. A better suitable material for wafer integration is molybdenum (Mo). Mo was shown to give good and uniform graphene growth [9, 10] and is CMOS compatible. It has a high melting point (~2600 °C), a thermal expansion coefficient closer to that of Silicon (Mo = 4.8 versus Si = 2.6 μm·m⁻¹·K⁻¹) than Ni and Cu. Finally, Mo is easy to remove in common etchants such as H₂O, H₂O₂ and HNO₃, making integration with CMOS easier.

Up to now, graphene growth by CVD has been prevalently focused on obtaining the crystal nucleation starting from the hydrocarbon gas sources, such...
as methane, acetylene, ethylene, benzene or hexane [6, 11], as well as liquid precursors, such as ethanol, methanol, 1-propanol or liquid hexane [6, 7, 11–14].

Only a few attempts for starting from solid state carbon precursors have been reported so far [15–17]. In particular, graphene growth has been demonstrated underneath thin-films catalyst [16, 17]. Other new methods for the synthesis of carbon nanomaterials, such as the chlorination of amorphous and 2D crystalline carbide, and the synthesis directly from an indecomposable solid carbon source, have been recently explored [18–22].

In this work, we present graphene grown on top of Mo from a solid amorphous carbon (a-C) precursor layer. We show MLG nucleation by using a solid phase reaction assisted only by annealing at 915 °C. We demonstrate that the proposed process generates high quality MLG on both stacks of Mo underneath or above the a-C layer.

2. Experimental sections

2.1. Material preparation

Silicon (1 0 0) wafers (p-type) with resistivity of 20–30 Ωcm covered by a 500 nm-thick thermally grown SiO2 film were used as base substrate. On top of the oxidized Si wafers, a double layer, either Mo on top of a-C or a-C on top of Mo, was deposited (see table 1 for details). The Mo and a-C layers were sputtered in a Veeco Nexus cluster tool at room temperature from targets having purity equal to 6N5 and 4N for Mo and C, respectively.

To grow graphene, we performed a thermal anneal up to 915 °C in an AIXTRON BlackMagic Pro. The anneal gas consisted of an Ar and H2 mixture at a pressure of 25 mbar. The temperature profile for the annealing process is illustrated in figure 1.

The temperature profile starts with a three stages slow ramp up to 915 °C in order to reduce thermal stress in the Si and Mo layers.

The first stage is the fastest one with a rate of 200 °C min⁻¹, rising from room temperature to 525 °C. It is followed by a slower ramp rate (50 °C min⁻¹) till 725 °C. For the third stage, the ramp up rate is 30 °C min⁻¹ and lasts until the final temperature (915 °C) is reached. A 1 min interval for temperature stabilization is included between the different ramp up stages. The growth is performed at 915 °C for different time windows, as summarized in table 2.

The cooling down rate is 25 °C min⁻¹ till 525 °C. At this point, the heater is completely switched off. Because of the thermal inertia, the cooling down has an exponential profile, as shown by the black line in figure 1.

The annealing was carried out in a mixture of Ar and H2. By varying the ratio of the two gases and/or the growth time, the influence of the gas atmosphere on the growth process (see table 2) was investigated.

In figure 2 the different initial layer stacks are depicted in panels (a) and (b), with a-C underneath and above the catalyst layer, respectively. The panels (c) and (d) schematically display the evolution of the layers in panels (a) and (b), respectively, due to the annealing process. The details of the physical growth process are addressed in the section 3.

Table 1. Layer stacks of Mo and a-C with respective thicknesses. In the last column, the sketches of the base structures are displayed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer 1</th>
<th>Thickness (nm)</th>
<th>Layer 2</th>
<th>Thickness (nm)</th>
<th>Schematic of layer stacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>a-C</td>
<td>500</td>
<td>Mo</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>a-C</td>
<td>40</td>
<td>Mo</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>Mo</td>
<td>50</td>
<td>a-C</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Sample 4</td>
<td>Mo</td>
<td>50</td>
<td>a-C</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>
X-ray photoelectron spectroscopy (XPS) was employed to investigate the formation of the Mo$_2$C during the anneal process. The XPS measurements were carried out in a Quantera SXM™ from ULVAC-PHI using monochromatic AlKα-radiation (25 W) and a take-off angle Θ of 45°. Concentration depth profiles were determined by alternating measurements and Ar ion bombardment, using 2 or 4 keV energy.

After growth, a FEI image corrected Titan Cube 80–300 kV delivers a cross-sectional analysis of the samples. Lamellae of about 12 µm for transmission electron microscopy (TEM) were prepared using a dual-beam Helios G4 CX focused ion beam-scanning electron microscope (FIB_SEM). To protect the area of interest (AOI), a thin layer of Pt was deposited on the AOI using electron beam induced deposition (EBID) method. To protect the sample during the TEM lamella preparation process, another layer of Pt of about 1200 µm was deposited using ion beam induced deposition (IBID).

3. Results and discussion

Figure 3 displays the Raman spectra captured on the substrates described in table 1. The top two panels (Sample 1 and Sample 2, figures 3(a)–(d)) show the Raman spectra on the Mo on a-C stacks. The bottom two panels (Sample 3 and Sample 4, figures 3(e)–(h)) refer to a-C on top of Mo stacks. In each panel, the spectra on the left side are recorded before the thermal anneal. The spectra on the right side show the results of the thermal anneal following Recipe #1 from table 2.

The spectra on the left side of each panel display a broad band around 1500 cm$^{-1}$ typical for amorphous carbon with a clear absence of any large-scale crystalline order [15, 16]. This band originates from the convolution of the defect related D-band, typically found at 1330 cm$^{-1}$ for the used laser wavelength, and the sp$^2$-carbon G-band at 1580 cm$^{-1}$ [23]. The broad band is more evident in figures 3(e) and (g). On the two samples with the metallic Mo layer on top (figures 3(a) and (c)), the Raman signals are partly quenched by the thin metal layer but are still clearly representative of an amorphous carbon layer.

The Raman spectra provide insight on the role of the solid precursor thickness on the growth process. The Raman spectra of all samples change after the anneal step. Sample 1, Sample 3 and Sample 4 present a graphitic signal whilst Sample 2 does not show any detectable signal even though the layers stack is similar to Sample 1. The only difference between Sample 1 and Sample 2 as well as between Sample 3 and Sample 4 is the thickness of the a-C layer (see table 1). These observations lead to conclude that the thickness of the solid precursor plays an important role in both the growth process and the final graphitic structure.

After the anneal, all samples with the exception of Sample 2 exhibit the D-band (~1330 cm$^{-1}$) and G-band (~1580 cm$^{-1}$). Compared to the overall absence of any lattice structure, argued from the spectra in figures 3(a)–(g), the splitting of the singular peak into two clear separate bands indicates a hexagonal sp$^2$ structure, although disordered to some extent [16, 23, 24]. Sample 1 and Sample 4 also present the sharp 2D peak at around 2700 cm$^{-1}$, typically associated to the graphite-like materials. For Samples 1 and Sample 4, the average full width half maximum (FWHM) measures 45 and 59 cm$^{-1}$, respectively. Hence, the rise of the 2D peak having a FWHM of a few tens of cm$^{-1}$ and the presence of D and G-peaks definitely prove the graphitization on the structures [25].

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Growth temperature (°C)</th>
<th>Growth time (min)</th>
<th>Composition of Ar/H$_2$ atmosphere (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>915</td>
<td>90</td>
<td>960/40</td>
</tr>
<tr>
<td>2</td>
<td>915</td>
<td>90</td>
<td>960/40</td>
</tr>
<tr>
<td>3</td>
<td>915</td>
<td>90</td>
<td>960/40</td>
</tr>
<tr>
<td>4</td>
<td>915</td>
<td>90</td>
<td>0/1000</td>
</tr>
<tr>
<td>5</td>
<td>915</td>
<td>90</td>
<td>0/1000</td>
</tr>
<tr>
<td>6</td>
<td>915</td>
<td>90</td>
<td>0/1000</td>
</tr>
<tr>
<td>7</td>
<td>915</td>
<td>90</td>
<td>1000/0</td>
</tr>
</tbody>
</table>
Noteworthy, the graphene-like signal on Sample 1 (figure 3(a)) and Sample 4 (figure 3(c)) demonstrates that a solid a-C source can be used to grow MLG. Somewhat surprisingly, the a-C can be located either underneath or above Mo film. At the same time, Sample 3 (figure 3(b)) displays how the stack details do affect the growth. A thick top carbon layer only results in the D and G bands splitting, indicative of the transition from a disordered structure to an arranged structure [23]. No clear graphitic structure is formed as this would have resulted in a 2D band.

Further insight in the material structure is provided by STEM (scanning transmission electron microscopy) and cross-sectional TEM (transmission electron microscopy) investigation on the lamellae prepared as described in the experimental section. Images acquired in different spots of the samples are reported in figure 4.
STEM and TEM images (figures 4(a)–(b)) show the overall structure of the sample just sketched in figure 2(c). Both images display the modifications of the initial layers of Mo and a-C. The a-C layer diffused inside the Mo film over the entire sample. This diffusion assisted by the elevated temperature formed Mo2C which is visible as the darker structures about 70 nm thick (figures 4(b) and (c)). Mo2C formation, discussed in more details in the supporting information (figure S1 (stacks.iop.org/TDM/6/035012/mmedia)), has been demonstrated by Gall and his group [26] and also recently during the growth on Mo by CVD [27]. In our case, once Mo2C was formed, the Mo broke up into nanocrystals, likely due to the low thickness of the initial Mo film (20 nm). Some of the Mo2C particles migrated through the entire a-C layer leaving graphitic planes in the wake [28]. The particles are clearly visible in figure 4(b) (see red circles). The migration of the Mo2C particles is even clearer in figure 4(c), where some facets of Mo2C formed inside the a-C layer are shown. The paths left along the wake during the migration of the Mo2C particles are again visible, sometimes appearing as needlelike Mo2C crystallites. A similar phenomenon, called metal-induced lateral crystallization, is encountered in the field of semiconductors [29].

The breakdown of the Mo film can be ascribed to the thin catalyst layer, being only 20 nm. We investigated a sample having a thicker Mo layer (100 nm) and we found no disruptions in the Mo film, regardless the unchanged capability to grow MLG (figure S2).

On top of the Mo2C (figure 4(c)), a graphitic layer was formed either during the anneal or after the segregation of C during the cooling phase. As claimed by Nakajima and co-authors, most likely the formation of the graphitic layer occurred during the annealing process [17]. a-C diffuses into Mo the layer and once the supersaturation of C is reached, the stable graphitic structures start nucleating on top of the formed Mo2C. Figure 4(d) is the close-up of the red square in figure 4(c). Above the Mo2C facets, two parts roughly separated by the yellow dashed line are visible (figure 4(d)). The portion below the line is characterized by clearly distinguishable fringes, having a thickness of about 10–15 nm. The fringes can be uniquely assigned to the grown MLG, as previously highlighted by the Raman spectra (figure 3(b)). The number of graphene layers is estimated to be 20–30, assuming the thickness of a single layer to be 0.4–0.5 nm [30]. Above the yellow line, no ordered structures are recognized. The amorphous material might come out from the residues of a-C after the anneal. The Raman spectra point out those contributions. If the same contributions were present in Sample 1, the Raman spectra would have been analogously affected. The clear absence of any peak in the range 1100–1600 cm$^{-1}$ leads to conclude that the disordered part on Sample 1 is formed after the growth process. The only possible source of amorphous material after the anneal step is therefore the Pt used for the lamella preparation.

To further understand the differences between Sample 1 and Sample 4, we analyzed both samples by AFM. The two surfaces were distinctly different (figure 5).

Sample 4 shows a similar behaviour as can be seen in figures 4(e)–(h). The STEM and TEM images show the modifications of the initial layers sketched in figure 2(d). Also in this sample, the diffusion of a-C into the Mo layer results in the Mo2C formation (figure S1). For Sample 4, on top of the Mo2C layer, a continuous film of MLG should be expected, as happens for Sample 1. Both figures 4(e) and (f) instead present agglomerated structures, which appear not homogeneously distributed on the surface. A close-up (figure 4(g)) displays a bulge with a height of roughly 50–60 nm. The location of the bulges on top of the Mo2C layer and the height comparable to the thickness of the initial a-C layer led to consider the bulges as agglomerations of the a-C film. These agglomerations originate from the anneal step. During the diffusion of C into the Mo and/or the segregation on top of the Mo2C to form the MLG, the a-C film does not remain continuous. The film fragmentation is probably due to the low thickness of the initial a-C layer (40 nm) (figure S3).

Figure 4(h) shows the magnification of part of the bulge enclosed in the red frame in figure 4(g). The yellow dashed line (figure 4(h)) splits the bulge roughly into two parts. Below the line, the fringes are immediately on top of Mo2C and the section of the layer is about 25 nm thick (~50 layers of graphene). Above the line, no ordered structures are recognized in the about 15 nm thick portion. The unorganized part might be the rest of the initial a-C layer which is not transformed into graphitic material. The thicknesses of Mo and a-C utilized for the experiments were comparable (table 1) and possibly not all a-C could diffuse into the Mo layer. The remaining a-C is left untransformed. The amorphous section in Sample 4 clarifies the origin of the disordered area in Sample 1. In both samples, the thickness of the amorphous parts is comparable. In Sample 4, however, we have seen that the disordered part comes from the residues of a-C after the anneal. In fact, the Raman spectra point out those contributions. The amorphous part on Sample 1 leads to conclude that the disordered part on Sample 1 is formed after the growth process. The only possible source of amorphous material after the anneal step is therefore the Pt used for the lamella preparation.

To further understand the differences between Sample 1 and Sample 4, we analyzed both samples by AFM. The two surfaces were distinctly different (figure 5).
As shown in figure 5(b), the material presents a roughness of about 20 nm which is in the same order of the Mo₂C crystals observed in the TEM images. AFM image (figure 5(b)) confirms that the thicker features are not homogeneously distributed on the surface and have heights of about 50 nm, as indicated by the profile in the inset. These features correspond to the blob-like structures observed in the TEM.

The outcomes discussed so far and especially the TEM images shed light on the physics of the growth
mechanism. Assisted by the elevated temperature, a-C diffuses into the Mo layer, as basically shown in figures 4(a) and (b). Bulk Mo2C is formed and the carbide serves as nucleating compound for the MLG precipitation on the top. As the solid a-C is the precursor both of the carbide and of the MLG, the amounts of precursor and catalyst matter. For instance, Sample 1 and Sample 2 have the same stack configurations but the thinner layer of a-C (40 nm) seems insufficient for the growth. All a-C is consumed for Mo2C formation as witnessed by the Raman spectroscopy on Sample 2 (figure 3(d)); nor graphitic nor a-C signal (figure 3(c)).

The proposed process is strengthened by comparing Sample 3 with Sample 4, with an a-C layer thicknesses of 40 nm or 500 nm above the Mo film (50 nm, see table 1). Sample 3 reveals only disordered hexagonal sp2 structures. Some graphitic layers might be formed but the large thickness of a-C (500 nm) prevents the detection of any graphitic signal at the interface with Mo.

When the solid carbon source is 40 nm, such as in Sample 4, we observed a-C partially dissolved inside the Mo layer and partially untransformed, as previously discussed.

In order to further address the role of the annealing time in the growth process, Recipes #1 was performed at two different times (indicated as Recipe #2 and Recipe #3 in table 2).

In figure 6 the average spectra obtained on the samples after these three recipes are compared. For sake of clarity, Sample 2 has not been reported, since no signal was detected on it, as previously shown.

For Sample 1 and Sample 3, substantial differences as function of annealing time are not immediately detectable. The FWHM of the 2D peak and the intensity ratio between 2D and G peak \((I(2D)/I(G))\) are generally the useful parameters to first discriminate between SLG and few layer graphene (FLG) or MLG [25]. By fitting the 2D peak of Sample 1 with a single Lorentzian, the FWHM(2D) equals 46 cm\(^{-1}\) proving the material to be MLG, as further settled by \(I(2D)/I(G)\) roughly equal to 1.6 [30]. The ratio between the D and G peaks, \(I(D)/I(G)\), is about 0.3 and demonstrates the high quality of the produced material, in close agreement with the findings obtained with the conventional CVD process [23, 25, 33].

It can be seen that a clear evolution of the Raman profile is observed for Sample 1. By increasing the annealing time, the material changes from disordered hexagonal sp2 structures (black line) to MLG plus a-C (green line). The rise and shaping of the 2D band provides the most prominent indication of the graphitization. After 30 min of annealing, there is no presence of the 2D peak, which starts appearing after 60 min and it is well defined after 90 min growth. Decreasing the anneal time from 90 min down to 5 min on Sample 1 still shows MLG growth with a quality similar to that reported in figure 6 for 90 min anneal. At a reduced anneal temperatures of 800 °C, we no longer observe any growth which is similar to our observations on CVD based MLG [34]. Figure 7 shows the comparison between the various anneal temperatures and times.

On Sample 1, the absence of any Raman fingerprint in panel figure 7(a) (black line) compared to the typical features present in figure 6(a) (red line) definitively proves that temperature value of 800 °C is not sufficient to grow MLG by the approach hereby presented. It is clear that both low temperature (800 °C) and shorter anneal time (5 min) produced the graphite clustering on Sample 3 and Sample 4 (figures 7(b) and (c)), as previously reported (see figure 3). Further investigations are required to explain if such temperature prevents Mo2C formation or if the diffusion of C into Mo is too slow at 800 °C, requiring a significantly longer anneal time.

The experimental data attest that not only MLG can be directly obtained by annealing the a-C layer but also that an anneal time as short as 5 min is enough for the growth.

Atmospheres during the annealing process were varied to discover a possible effect of the gases on the growth mechanism. Since the etching power of H2 on graphene during the conventional CVD process is well known, especially in presence of TMAs [7], the mixture of Ar and H2 used in the recipes so far described was replaced by only H2 or Ar (last five recipes in table 2). The obtained results unclose that the growth
mechanism was not affected by the gas composition used (figure S5).

The growth mechanism worked for two configurations, i.e. a-C below and above Mo. In table 3 the features of the material presented in this paper are compared with those of material we synthesized in the Aixtron Black Magic Pro through the commonly used CVD process adopting the conventional hydrocarbon source [35–37]. In order to make the comparison more reliable with the growth by CVD, a growth time of 90 min has been selected, although we proved that there is no significant variance of the Raman parameters by using the different annealing times.

The materials grown with the different recipes are remarkably similar. In particular, looking at Sample 1 prepared through Recipe #4, the narrower 2D peak and the higher value of I(2D)/I(G) with respect to Recipe #1 indicate the synthesis of a slightly thinner material. We come to the same conclusion by comparing the values of FWHM(2D) and I(2D)/I(G), especially those related to Sample 1, with the material we prepared by CVD. Our result suggests that the process with a-C is slower than the commonly used CVD, since in both processes...
we have adopted the same growth time (90 min). Also for Sample 4 the overall substantial equivalence with the conventional CVD process is underlined, showing a maximum variation of 15% of the FWHM(2D). For Sample 4, we did not take into account the ratio I(D)/I(G) for the comparison of the results. In fact I(D)/I(G) can be a misleading parameter since we have proved that for Sample 4 the Raman spectrum contains contributions of both MLG and a-C residues.

The reported outcomes indicate that the growth through the annealing of solid phase carbon really has potential to provide 2D material having quality comparable and even higher than those grown by the CVD process adopting the usual hydrocarbon sources.

### 4. Conclusions

In this work, we have investigated the growth mechanism of MLG by thermal anneal of a solid a-C source in the presence of a Mo catalyst layer.

We proved that MLG growth happens with the catalyst layer sputtered either above or below an a-C layer. The growth mechanism consists of the diffusion of a-C inside the catalyst layer, followed by C segregation and MLG formation on top of Mo layer.

The highest quality of MLG, proved through Raman spectroscopy and cross-sectional TEM, was obtained with a 20 nm-thick Mo layer deposited on a 500 nm-thick a-C film. We found that the quality is at least as good as that obtained in conventional CVD with gaseous hydrocarbon sources, as can be seen from Raman results. We demonstrated that the minimum temperature to grow FLG is 915 °C. The annealing time was varied, discovering that MLG are achieved already after 5 min of anneal. We successfully demonstrated that the atmosphere during the anneal does not affect the material features. The presented findings provide a jolt towards a possible alternative for CVD based mechanisms.

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### ORCID iDs

Filiberto Ricciardella  [https://orcid.org/0000-0002-9669-5649](https://orcid.org/0000-0002-9669-5649)

Sten Vollebregt  [https://orcid.org/0000-0001-6012-6180](https://orcid.org/0000-0001-6012-6180)

Majid Ahmadi  [https://orcid.org/0000-0003-2321-3060](https://orcid.org/0000-0003-2321-3060)

### References

[7] Seah C M, Chai S P and Mohamed A R 2014 Carbon 70 1
[12] Li X et al 2009 Science 324 1312

### Table 3. Values of FWHM(2D), I(D)/I(G) and I(D)/I(G) determined by the Raman spectra. These values are compared with those obtained by the standard CVD process.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>FWHM (2D) (cm⁻¹)</th>
<th>I(D)/I(G)</th>
<th>I(D)/I(G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>#1</td>
<td>47</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>#4</td>
<td>42</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>#7</td>
<td>49</td>
<td>1.2</td>
</tr>
<tr>
<td>Sample 4</td>
<td>#1</td>
<td>59</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>#4</td>
<td>63</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>#7</td>
<td>62</td>
<td>1.0</td>
</tr>
<tr>
<td>Reference [35]</td>
<td>Conventional CVD</td>
<td>55</td>
<td>0.9</td>
</tr>
</tbody>
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[33] Ferrari A C and Basko D M 2013 Nat. Nanotechnol. 8 235
[34] Ricciardella F, Vollebregt S, Polichetti T, Alfano B, Massera E and Sarro P M 2017 Proceedings 1 445