Bifunctional catalytic effect of Mo$_2$C/oxide interface on multi-layer graphene growth

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The role of the Mo$_2$C/oxide interface on multi-layer graphene (MLG) nucleation during a chemical vapor deposition (CVD) process is investigated. During the CVD process, MLG growth is only observed in the presence of a Mo$_2$C/SiO$_2$ interface, indicating that the chemical reactions occurring at this interface trigger the nucleation of MLG. The chemical reaction pathway is explained in four steps as (1) creation of H radicals, (2) reduction of the oxide surface, (3) formation of C–C bonds at O–H sites, and (4) expansion of graphitic domains on the Mo$_2$C catalyst. Different Mo$_2$C/oxide interfaces are investigated, with varying affinity for reduction in a hydrogen environment. The results demonstrate a catalyst/oxide bifunctionality on MLG nucleation, comprising of CH$_4$ dehydrogenation by Mo$_2$C and initial C–C bond formation at the oxide interface.

Graphene is a two-dimensional material with unique properties such as high carrier mobility$^1$, high strength$^2$ and high optical transparency$^3$, which is advantageous for application areas such as transistors$^4$, solar cells$^5$, sensors$^6$, and batteries$^7$. Chemical vapor deposition (CVD) is currently the most promising method to synthesize large scale graphene for industrial applications$^8$$^9$. Mo$_2$C, from the transition metal carbide (TMC) family, is a leading candidate as a catalyst for uniform mono/multi-layer graphene synthesis due to its noble metal like catalytic activity, low cost, and high thermal stability$^{10}$$^{12}$.

In our previous work, the growth of multi-layer graphene (MLG) was linked to the presence of pinholes in Mo$_2$C thin films$^{13}$. Such pinholes could expose the underlying oxide, which may play an important role in the graphene synthesis process. It is known from the field of catalysis that underlying oxide, commonly known as the “support layer”, can actively participate in catalytic reactions$^{14}$$^{19}$. As an example, the influence of the support layer on carbon nanotube (CNT) synthesis is widely studied$^{17}$$^{19}$, and it is found that the oxide interface causes initial CNT nucleation$^{18}$$^{20}$. It is stated that ordered carbon formation on oxide is triggered by hydroxide and oxygen species$^{18}$$^{20}$, which can be potentially important for MLG synthesis. Furthermore, Mo$_2$C is a catalyst that shows different catalytic activity depending on the oxide under-layer (support) used$^{21}$$^{22}$. Mo$_2$C in combination with ZSM-5 zeolite supports causes aromatization of CH$_4$, whereas this is not the case for only Mo$_2$C or ZSM-5 separately$^{23}$. This shows that both the catalyst and neighboring oxide can play a role in graphene synthesis, which to our knowledge has not yet been investigated.

In this study, we will demonstrate that the interface between pinhole-free Mo$_2$C and SiO$_2$ is triggering MLG nucleation upon the CVD process. We will introduce a model for explaining the MLG nucleation by catalyst/oxide bi-functionality. This model is based on the complementary role of MoO$_x$ ($x=0$–0.5) for CH$_4$ dehydrogenation and SiO$_2$ for C–C bond formation after reduction with hydrogen. We will test this model by performing the CVD process in absence of hydrogen gas, as well as using different oxide (TiO$_2$, Al$_2$O$_3$, MgO) interfaces, in which we expect a dependence of MLG nucleation on the oxide reducibility. The outcome of this study shows that the catalyst-oxide interface interaction is crucial for understanding the MLG synthesis on Mo$_2$C thin films.

Methods

In this section, the MLG synthesis process will be explained in three parts. In the first part, the thin film deposition process flow of Mo catalysts on Si/SiO$_2$ substrates will be given. This process is known to result in pinhole-free Mo$_2$C, which does not yield MLG growth upon subsequent CVD processing$^{13}$. In the second part, the deposition/patterning of oxides will be explained in order to create an interface which is expected to play a role...

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in MLG synthesis. In the final part, the applied CVD process for MLG growth, and characterization methods for analyzing synthesized MLG, will be described.

To remove possible surface contamination and the native oxide layer on top, p-type (100) single side polished silicon wafers are cleaned with ozone steam and HF, sequentially. To prevent Mo₂C/Si interdiffusion, a 300 nm thermal SiO₂ layer is grown on top of Si, by means of a dry oxidation process at 1100 °C. Directly before the sputtering process, the samples are cleaned with HNO₃ to remove any organic contaminants on the sample surface. For the majority of samples, a Mo layer is deposited onto the SiO₂ layer using magnetron sputtering, resulting in a pinhole-free Mo₂C layer upon the CVD process described in ref 13. A nominal Mo layer thickness of 70 nm was used for all samples, because in separate experiments it was shown that thinner Mo layers (with pinholes) result in graphene layers with significantly higher D/G ratios. This is explained by the strong reduction of the Mo crystallite size for thinner layers, which is expected to correlate to the formation of more pinholes and therefore significantly higher MLG nucleation density. In addition, ‘standard’ MLG thickness for 70 nm Mo layer (with pinholes) is around 11 nm corresponding to 32 layers, according to low energy ion scattering (LEIS) measurements (not shown here. After Mo deposition, a specific oxide top layer was deposited onto each sample using reactive sputtering. All sputter depositions are carried out in the same UHV deposition chamber, with a target to substrate distance of 300 mm and a base pressure of 10⁻⁸ mbar, using the conditions given in Table 1.

To test the impact of an exposed Mo/oxide interface on MLG growth, several procedures were developed based on optical UV lithography and including various wet etching/lift off steps, yielding a patterned oxide layer with lines and line spaces ranging from 1 to 10 micron, with length scales chosen similar to typical graphene domain sizes observed in previous studies. For creating an exposed Mo/SiO₂ interface, two methods where developed. One method involves patterning the SiO₂ layer before the deposition of Mo, as schematically shown in Fig. 1a. To fabricate a line step significantly higher than the thickness of the Mo layer, the thermal SiO₂ layer is wet etched by buffered hydrofluoric acid (BHF) for 2 min resulting in a step of 150 nm. A Mo layer is then deposited at an off-normal angle, inducing a “shadow” in the deposited area on one side of the steps (shown by a black circle, Fig. 1a), leading to an exposed interface between Mo and SiO₂. Another method to create an exposed Mo/SiO₂ interface involves a lift-off process. Here, a ‘lift-off resist’ (LOR) and a top regular photoresist are developed. One method involves patterning the SiO₂ layer before the deposition of Mo, as schematically shown in Fig. 2a. To remove possible surface contamination and the native oxide layer on top, p-type (100) single side polished silicon wafers are cleaned with ozone steam and HF, sequentially. To prevent Mo₂C/Si interdiffusion, a 300 nm thermal SiO₂ layer is grown on top of Si, by means of a dry oxidation process at 1100 °C. Directly before the sputtering process, the samples are cleaned with HNO₃ to remove any organic contaminants on the sample surface. For the majority of samples, a Mo layer is deposited onto the SiO₂ layer using magnetron sputtering, resulting in a pinhole-free Mo₂C layer upon the CVD process described in ref 13. A nominal Mo layer thickness of 70 nm was used for all samples, because in separate experiments it was shown that thinner Mo layers (with pinholes) result in graphene layers with significant higher D/G ratios. This is explained by the strong reduction of the Mo crystallite size for thinner layers, which is expected to correlate to the formation of more pinholes and therefore significantly higher MLG nucleation density. In addition, ‘standard’ MLG thickness for 70 nm Mo layer (with pinholes) is around 11 nm corresponding to 32 layers, according to low energy ion scattering (LEIS) measurements (not shown here. After Mo deposition, a specific oxide top layer was deposited onto each sample using reactive sputtering. All sputter depositions are carried out in the same UHV deposition chamber, with a target to substrate distance of 300 mm and a base pressure of 10⁻⁸ mbar, using the conditions given in Table 1.

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After fabrication of samples with exposed Mo/oxide interfaces, a CVD process is applied to all samples using a cold wall reactor system in presence of CH₄, Ar and, H₂ gasses at 1000 °C for 35 min, using the same parameters from our previous study⁵. To test the role of hydrogen in the MLG growth process, additional experiments were done where the same CVD process was applied, but without H₂.

To characterize the structure of CVD deposited carbon, Raman measurements are performed, using a WITec alpha 300 system with a 0.9 NA objective and a 532 nm wavelength laser. The power of the laser is adjusted to 1 mW to avoid damage to graphene. The Raman spectra are recorded over a 10 by 10 micro meter area, and averaged for 9 spectra. I_D/I_G ratios of graphene layers are obtained by processing of the Raman data with a MATLAB script using Lorentzian peak fitting and normalization. The surface topography and elemental contrast imaging are carried out using a Zeiss MERLIN HR-SEM system with a voltage of 1.4 kV for improved surface sensitivity and in addition an EsB detector is used to make the nano-scale composition visible.

**Results and discussion**

In our earlier work⁵, it is shown that the nucleation and growth (or absence thereof) of MLG on Mo₂C was strongly related to the presence (or absence) of pinholes in Mo₂C. From this observation, we hypothesize that the Mo₂C/SiO₂ interface can play an important, bifunctional, role by catalyzing different reactions for MLG and in addition an EsB detector is used to make the nano-scale composition visible.

**Effect of Mo₂C/SiO₂ interface on MLG nucleation.** To create a system where within one sample both exposed and unexposed Mo₂C/SiO₂ interfaces are present, the structure as defined in Fig. 1a was prepared and subsequently exposed to the CVD process.

In Fig. 2a, c the cross-section SEM images of the left and right side of the step after the CVD process is presented, showing (a) a Mo₂C layer with an exposed Mo₂C/SiO₂ interface on the left side of the step, and (c) a

| Material | Deposition pressure (E-4 mbar) | Ar (sscm) | O₂ (sscm) | Current (A) | Voltage (V) | Target name (4 in.), supplier purity (%) |
|----------|-----------------------------|----------|-----------|-------------|------------|----------------------------------------|
| Mo       | 8.5                         | 30       | 0         | 1           | 378        | Mo, Robeko, 99.95                      |
| SiO₂     | 7.8                         | 20       | 20        | 0.25        | 306        | Si, Sindhauser, 99.999                  |
| TiO₂     | 7.2                         | 18       | 18        | 1           | 570        | Ti, Robeko, 99.5                      |
| Al₂O₃    | 4.2                         | 11       | 11        | 1.5         | 386        | Al, Sindhauser, 99.99                  |
| MgO      | 7.9                         | 20       | 20        | 1           | 172        | Mg, Sindhauser, 99.95                  |

Table 1. Overview of the used sputtering parameters.
continuous Mo\(_2\)C layer on the right side of the step. Based on our hypothesis, MLG growth is expected where the Mo/SiO\(_2\) interface is exposed to the CVD process, as sketched in Fig. 2b. In Fig. 2d, the elemental contrast mode of SEM indeed confirms the presence of carbonaceous species (dark colour) centred on the exposed interface. The Raman spectrum is shown in Fig. 2e, confirming the characteristic peaks of MLG which are known as D, G, 2D peaks. This clearly suggest that MLG growth is initiated at the exposed Mo\(_2\)C/SiO\(_2\) interface.

In the following section, we will propose a model explaining the MLG nucleation mechanism taking place exclusively at the exposed Mo\(_2\)C/SiO\(_2\) interface.

**MLG nucleation model.** According to the d-band model, Mo has a strong interaction towards adsorbates such as CH\(_4\) leading to formation of a molybdenum carbide\(^{24}\), which is also known to occur upon the CVD process used for MLG synthesis\(^{10,11}\). In-situ formed Mo\(_2\)C is generally considered as a catalyst for the MLG synthesis process, since it has noble metal like catalytic activity due to its modified band structure by compound formation\(^{10,11}\).

In this section, a chemical reaction pathway will be proposed for MLG nucleation on Mo\(_2\)C, with particular emphasis on the role of the exposed Mo\(_2\)C/SiO\(_2\) interface, as indicated in Fig. 3.

**Step 1: Formation of radicals.** The first step of MLG nucleation is the adsorption and subsequent dehydrogenation of CH\(_4\) on the Mo surface. Mo has a high reactivity towards dehydrogenation of CH\(_4\) due to its d-band structure, resulting in formation of C\(^*\) and H\(^*\) radicals.

**Step 2: Diffusion of radicals.** The reaction pathway continues with the diffusion of C\(^*\) and H\(^*\) radicals, formed in the previous step. C\(^*\) species diffuse into the Mo layer to form a stable carbide structure via Mo–C chemical bond formation\(^{10,11}\). Although some of the H radicals can diffuse into the Mo layer from grain boundary defects, this is expected to be minimal due to its low hydrogen permeability\(^{25,26}\). A part of the H\(^*\) species is expected to diffuse over the Mo\(_2\)C surface and onto the SiO\(_2\) surface, known as 'Hydrogen spillover'\(^{27}\) (Fig. 3, Step 2). These diffused atomic H\(^*\) species can cause a reduction of SiO\(_2\), especially at temperatures as high as 1000 °C\(^{27,28}\) causing activation of surface O–H sites.
Step 3: Formation of graphitic nuclei. Once the Mo₂C catalyst is formed, the generation of CHₓ⁺ radicals will continue on the catalyst surface via dehydrogenation of CH₄ [23]. These CHₓ⁺ radicals can be adsorbed chemically on SiO₂ surfaces at the interface through O–H sites, created in the previous step. This results in graphitic carbon formation via C–C coupling (Fig. 3, Step 3), which is a commonly known mechanism for graphene nucleation on SiO₂ substrates [29–31].
Step 4: Expansion of MLG domains. Once graphitic nuclei form at the interface between MoC and SiO2, MLG domains expand dominantly onto the MoC surface since the graphene growth rate on SiO2 is generally orders of magnitude slower.23,25

In summary, the MLG nucleation model proposed here is effectively driven by the MoC/SiO2 bi-functionality, where the oxide layer promotes the initial C–C bond formation whereas MoC causes CH4 dehydrogenation leading to the creation of radicals and expansion of MLG domains on its surface. Similar phenomena have also been reported for CNTs, where the oxide interface caused initial nucleation of CNTs and further growth continued on the catalyst by attachment of C species to the edge of the graphitic nuclei.18 In the following section, the critical assumptions of the model based on support layer bi-functionality (steps 2 and 3) will be validated.

Hydrogen spillover impact on MLG growth. In this section, we aim to study the importance of hydrogen spillover on the MLG growth process. In the MLG nucleation model in step 1, the expected source of the spillover H radicals is either the dehydrogenation of CH4 (CH4 → CH, CH → CH → C), formed upon the transition of Mo to MoC, or cracking of H2 (H2 → H* + H*) during the CVD process. To investigate the role of H2 in the creation of OH sites (and thereby being responsible for the MLG nucleation), experiments were carried out with and without hydrogen gas.

To fabricate a sharp Mo/SiO2 interface, two identical samples are prepared using lithography and lift-off processes. (See more details on the experimental section, Fig. 1b). The first sample is used as a reference in which our standard CVD process is applied (with Ar, H2, and CH4 gasses), whereas, for the second one, the CVD process is applied in absence of H2 gas, as shown schematically in Fig. 4a, b. The arrows indicate the transport (“spillover”) from Mo2C towards SiO2.

In Fig. 4c, d, the Raman spectra after the CVD process are shown. For both samples, D, G, and 2D peaks typical for MLG growth are observed, suggesting that CH4 dehydrogenation upon carbide formation creates sufficient H radicals for MLG nucleation via spillover (MLG nucleation model, step 2). While the G and 2D peaks exhibit similar I2d/Ig ratios for both samples, the Id/Ig ratio is reduced significantly in absence of H2 gas in the CVD process (Fig. 4e). A lower Id/Ig ratio in the MLG growth process without H2 gas indicates the formation of larger domains, which suggests fewer nucleation sites.

Reduction of the support layer. An critical step in the proposed model is the creation of OH sites through reduction of the oxide layer by H2. To investigate the importance of the oxide reduction step, we compare samples with different oxides (SiO2, TiO2, Al2O3, MgO), chosen based on their difference in reducibility. Specifically, the order of reducibility in an atomic hydrogen environment is expected to be SiO2 > TiO2 > Al2O3 > MgO, with energies −135,568 > −120.763 > −53.733 > −15.632 kJ/mol O228 with respect to their Gibbs free energy at 1000 K.

For interface formation, the oxide line patterns were created on top in order not to affect MoC crystallinity. A patterned surface with Mo/oxide interfaces was created for all samples using lithography and BHF wet etching (for more details, see experimental section Fig. 1c). Except for the sample with the MgO layer, all samples are patterned with a high yield. We believe that the sample with MgO continued to etch in the rinsing water after the BHF etching step, therefore only local patterns on sample could be analyzed.

In Fig. 5a–c, the Raman spectra after the CVD process are shown. Raman spectra indicate that sample with SiO2 lines showed strong MLG growth, whereas sample with TiO2 lines showed patchy growth and no growth is observed for the sample with Al2O3 lines. MLG growth is observed for SiO2 lines with the presence of D, G, and 2D peaks, showing similar spectra when compared to the lift-off patterned sample. The smaller appearance of the 2D peak for TiO2 suggests patchy deposition. No appearance of the 2D peak for Al2O3 indicates that there is no deposition of graphene. The local MgO patterns could not be traced back using Raman microscopy and thus no Raman spectra could be recorded. The Raman results clearly indicate that the reducibility of the oxide has a strong impact on graphene growth.

In order to semi-quantify the amount of carboneous species, the samples are analyzed simultaneously with the topography/elemental contrast mode of SEM, resulting in side-by-side images (Fig. 5d–g). Here, the elemental contrast mode shows the oxides and the carboneous species with darker contrast caused by their relatively low atomic number compared to the Mo-containing catalyst. The highest amount of carbon deposition is observed for SiO2 with dark contrast in between the lines. A smaller amount of carboneous deposition is observed on the edges of TiO2 lines. On Al2O3 and MgO samples, the carbon species are not observed. These SEM images correlate well with the observations from Raman, regarding the relation between oxide reducibility and graphene growth. These results therefore support our MLG nucleation model in which oxide reduction is a key step in creating OH sites required for triggering MLG nucleation.

The observed difference between SiO2 and TiO2 illustrated in Fig. 5a, b also suggests that the chemical reactivity for these oxides towards graphitization might be different, which is caused by a difference in the number of reactive sites and/or its strength.36,37 In addition, the generation of intermediate volatile (reaction) products such as Si–O38, and Si–H39, may lead to accumulation of graphitic carbon, similar to the graphene growth on SiC substrates.39–41
Conclusions
In this report, the active role of the Mo$_2$C/oxide interface on MLG nucleation is shown experimentally. A MLG nucleation model is proposed based on sequential chemical reactions, namely the formation of H species via CH$_4$ dehydrogenation/H$_2$ cracking, the migration of H species on the SiO$_2$ surface (spillover), the reduction of the SiO$_2$ surface, the activation of C–C bonds at O–H sites (as discussed in STEP 3 - MLG nucleation model), and the expansion of graphitic domains onto Mo$_2$C. It was shown that the dehydrogenation of CH$_4$ is already sufficient to supply the H* species required for oxide reduction, whereas additional H* through cracking of H$_2$ likely only increases the number of nucleation sites and reduces domain sizes. The Mo$_2$C/oxide bi-functionality is further studied by using different oxide layers with varying reducibility. Increased reducibility leads to increased graphene growth, confirming the importance of the role of oxide reduction in the proposed model. The results shown here contribute to unraveling the role of the catalyst/support interactions that take place in graphene synthesis, as such the bifunctional catalytic effect of the oxide under layer. This could be also relevant for other catalyst/support combinations, yet more research is needed to deeper understand bifunctional chemical reactions at the atomistic level.

Figure 4. Schematic images showing the H spillover during the CVD process for (a) standard CVD process, (b) CVD process in absence of external H$_2$ gas. Corresponding Raman spectra depicting the MLG growth for both samples given as (c) sample with H$_2$ gas in standard CVD process and (d) without, showing a difference in D peak. (e) Raman spectra zoomed in to D-peak region, comparing the $I_d$/I$_g$ ratios of the two samples, where for clarification a guide to eye was added (green line).
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Author contributions
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Competing interests
The authors declare no competing interests.

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