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Thermodynamic analysis of graphene CVD grown on liquid metal: Growth on liquid metallic gallium or solid gallium oxide skin?

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HIGHLIGHTS

- There have been reports of successful CVD growth of graphene on liquid Ga.
- Stability of Ga_2O_3 vs liquid Ga has been evaluated using thermodynamic analysis.
- A Ga_2O_3 skin should have been present on liquid Ga during several of these reports.
- The claimed graphene layers have grown on a solid Ga_2O_3 skin rather than on liquid Ga.
- Presence of a solid oxide skin alters the growth mechanism of graphene on liquid metals.

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ABSTRACT

A number of recent publications have reported liquid gallium to have an extraordinary catalytic activity for chemical vapor deposition (CVD) of graphene, enabling the growth of high-quality graphene on its surface even below 600 K. Our presented thermodynamic analysis however, indicates that during several of these experiments, an atomically thin gallium oxide layer should have covered the liquid gallium. This means that graphene should have actually grown on the solid oxide skin rather than on the liquid metal. This suggests a more complex mechanism for graphene growth on liquid gallium than what is currently considered in the community.

1. Introduction

Chemical vapor deposition (CVD) is one of the most promising methods for mass production of high-quality graphene. It involves the dissociation of a hydrocarbon precursor gas on a catalyst surface (*i.e.* dehydrogenation), where the released carbon atoms join to form a graphene layer (*i.e.* graphitization) [1,2]. One famous example is the dissociation of methane on a solid copper surface at about 1300 K [3]. The CVD gas also often contains argon as a background carrier gas and hydrogen as a reducing agent to avoid oxidation of the catalyst by the oxygen-containing impurities in the CVD gas and to tune the thermodynamics and kinetics of graphene growth [4].

Much effort has been put into simultaneously improving the graphene growth speed, its domain size, and its structural quality. In 2012, Geng et al. found that CVD of graphene on a liquid catalyst (in this case liquid copper at about 1370 K) enables the growth of significantly larger graphene domains with less defect density [5]. The naturally smooth, homogeneous, and isotropic liquid surface reduces the nucleation density of graphene flakes, while higher atomic mobility on the liquid leads to a faster flake growth. Hence, the produced graphene domains are significantly larger than the ones grown on solid catalysts. In addition, the absence of pinning sites and frictional forces on a liquid surface allows the graphene single-crystal flakes to grow freely according to their ideal form, decreasing their structural defects significantly.

Meanwhile, it is of great interest to lower the graphene CVD temperature, without compromising the quality and growth speed of the produced graphene. This can lead to a more efficient and economical graphene production process. One approach is to use a catalyst with higher activity, which can lower the energy barriers for the rate-limiting dehydrogenation or graphitization steps. For example, on solid nickel, which is a more active catalyst than solid copper, graphene can be grown at temperatures as low as 900 K [6]. Thus, much effort has been put into

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finding liquid catalysts that can activate graphene formation at temperatures lower than the copper melting point.

In 2013, Ding et al. [7] and Wang et al. [8] reported the first CVD growth of high-quality graphene on liquid gallium at 1273 K and 1293 K, respectively. Gallium already melts at 302.9 K and liquid gallium is known to be an active catalyst for graphitization of amorphous carbon [9,10]. This has been attributed to the fact that liquid gallium can dissolve more than 50 at% carbon on its surface, even though carbon solubility in the bulk is close to zero [11].

In 2015, Hiyama et al. reported the first low-temperature growth of graphene on liquid gallium [12]. This was achieved using preexisting graphene nuclei to bypass the barrier for graphene nucleation. The growth happened at the interface between a gallium drop and a sapphire substrate. In addition, a significantly more dilute methane concentration was used (0.01–0.001 of the one of Ding et al.) [7]. This reduces the carbon release rate to match the slow graphitization rate at reduced temperatures, otherwise the extra carbon atoms would deposit as amorphous carbon. In this way, good-quality graphene ($I_G/ I_D \geq 3$ in the acquired *ex situ* Raman spectra) could be grown at temperatures as low as 773 K.

In 2017, Fujita et al. reported the possibility of lowering the growth temperature of graphene on liquid gallium down to 373 K [13]. While in the three former reports, the CVD has been performed under atmospheric pressures conditions (APCVD) of 0.5–1.0 bar, Fujita et al. used dilute methane gas in low-pressure CVD (LPCVD) conditions of 2.0×10^{-4} bar total pressure.

For the case of solid or liquid copper catalysts, adding hydrogen in the CVD feedstock has been found to be essential in producing high-quality graphene [14]. Hydrogen helps reducing the surface metal oxide layer during the annealing stage and prohibits oxide formation during the graphene growth and cool-down stages. Curiously, to the best of our knowledge, there has been no report indicating the benefit of hydrogen addition to the CVD feedstock for graphene growth on liquid gallium. In fact, Ding et al. have expressed that they achieved the best graphene quality when no hydrogen was added to the feedstock [7]. Hydrogen is absent in all known low-temperature graphene growth recipes on liquid gallium [12,13]. There has even been no mentioning of an annealing step in the presence of hydrogen to remove the potential oxide layer on liquid gallium, before the graphene growth step.

This is important because it is well known that upon exposure to an oxygen-containing gas, most metals, including gallium, will quickly form an atomically thin (2D) oxide layer on the surface via a self-limiting reaction [15]. Even if one can avoid the contact of metal with air during handling, the minor oxygen contamination present in the CVD furnace is still enough to form an atomically thin oxide layer on the metal in a matter of seconds. For example, even a 6N-pure argon carrier gas contains ~ ppm level of oxygen-containing impurities. In addition, most of the CVD reactors used for graphene growth research worldwide are not vacuum-compatible, and minor air residues and leaks are always present in such systems. A background oxygen pressured of more than 10^{-6} mbar (corresponding to more than one Langmuir exposure) in common CVD systems will create about a monolayer of oxide in less than 1 s.

The first atomic layer of oxide can grow very fast because of the direct contact between the metal and oxygen molecules. However, for the oxide to grow thicker, either the oxygen atoms should diffuse through the oxide towards the oxide/metal interface or metal atoms should diffuse towards the gas/oxide interface. As the oxide layer acts as a barrier against these diffusion processes (especially at low temperatures where the diffusion is suppressed), the oxide layer remains atomically thin in the time scales relevant for the handling of metals in lab conditions [16,17]. Such a thin oxide layer is often not noticeable by naked eye.

Two types of gallium oxide are known: gallium (I) monoxide (Ga_2O) is known to decompose above 1073 K, but gallium (III) trioxide (Ga_2O_3) is stable at higher temperatures and only melts at 2079 K [18]. This raises the question whether the reported graphene growths on gallium had actually happened on the liquid metal or on a solid metal oxide overlayer.

Another piece of information comes from the recent findings in the field of catalysis. It has been observed that for the dehydrogenation of hydrocarbons (*e.g.* alkane conversion to alkene), metallic gallium shows virtually no catalytic activity, while the oxidized Ga^{3+} ion effectively catalyzes the reaction [19,20]. Can the fact that gallium has been found to be an excellent catalyst for graphene formation at low temperatures (especially in the absence of hydrogen) be related to the presence of an unnoticed gallium oxide layer on the liquid metal?

While the best way to verify the presence of an oxide layer on liquid gallium is *in situ* microscopy and spectroscopy during the CVD process [21], high corrosivity of gallium has been a roadblock against performing such experiments. In the absence of an *in situ* monitoring technique compatible with gallium, evaluating the thermodynamic stability of gallium oxide can provide valuable insights about the expected composition of the gallium surface under CVD conditions.

2. Methods

Standard formation Gibbs free energies for Ga_2O_3 (solid), Ga_2O (gas) [22], H_2O (gas), CH_4, CO, and CO_2 [18] have been used to calculate the standard reaction Gibbs free energies of oxide reduction, from which one can evaluate the reaction equilibrium temperatures. Here, standard conditions correspond to a partial pressure of 1 bar for gaseous species or unit activity for condensed phases.

3. Results

Fig. 1a shows the Gibbs free energy of several gallium oxide reduction reactions as a function of temperature, while Fig. 1b and c shows their equilibrium temperature as a function of partial pressures of different gas components in the CVD feedstock. The partial pressures and activities are selected to match their rough (order of magnitude) values during typical CVD experiments using feedstock gases with 6 N purity. The plots have been calculated using the fits of Gibbs free energy data in the temperature range of 300–1300 K, which encompasses the range of reported graphene CVD temperatures on gallium.

For gallium oxide reduction to metallic gallium, the limiting step is found to be the reduction of Ga_2O_3 to Ga_2O (solid lines), as the Ga_2O sub-oxide has a low stability and can easily be reduced to metallic gallium (dashed lines). Our thermodynamic analysis shows that direct dissociation of Ga_2O_3 to Ga_2O is not feasible below 1300 K (solid black line). As expected, the presence of H_2 in the feedstock can lower the onset of Ga_2O_3 reduction (solid magenta line). At a H_2 partial pressure of 10 mbar (its order of magnitude value in typical graphene CVD recipes), the onset of Ga_2O_3 reduction is ~1147 K.

Surprisingly, methane is found to be a stronger reducing agent for Ga_2O_3 than hydrogen. The most thermodynamically favorable reduction path by CH_4 is found to be via CO and H_2 formation (solid dark green line). During the growth stage, for a methane partial pressure of 1.0 mbar (the upper limit for typical graphene CVD recipes) and in absence of H_2 (partial pressure of 1×10^{-6} bar corresponding to the order of impurity level in 6 N gases), a temperature of at least ~691 K is needed for the onset of Ga_2O_3 reduction. At the presence of 10 mbar hydrogen during the growth stage, the onset of Ga_2O_3 reduction by CH_4 would be higher, *i.e.* ~895 K.

Meanwhile, methane dissociation on gallium (metal or oxide) leads to graphene formation during the growth stage (dotted black line). In the presence of carbon (graphene), another possible mechanism for gallium oxide reduction is via oxidation of graphene, producing CO or CO_2 (blue lines). Ga_2O_3 reduction by graphene via CO formation is more favorable and can happen at temperatures as low as ~1009 K (solid dark blue line).

Table 1 shows the reported graphene growth recipes on liquid gallium in the literature, known to the authors. Our calculated equilibrium

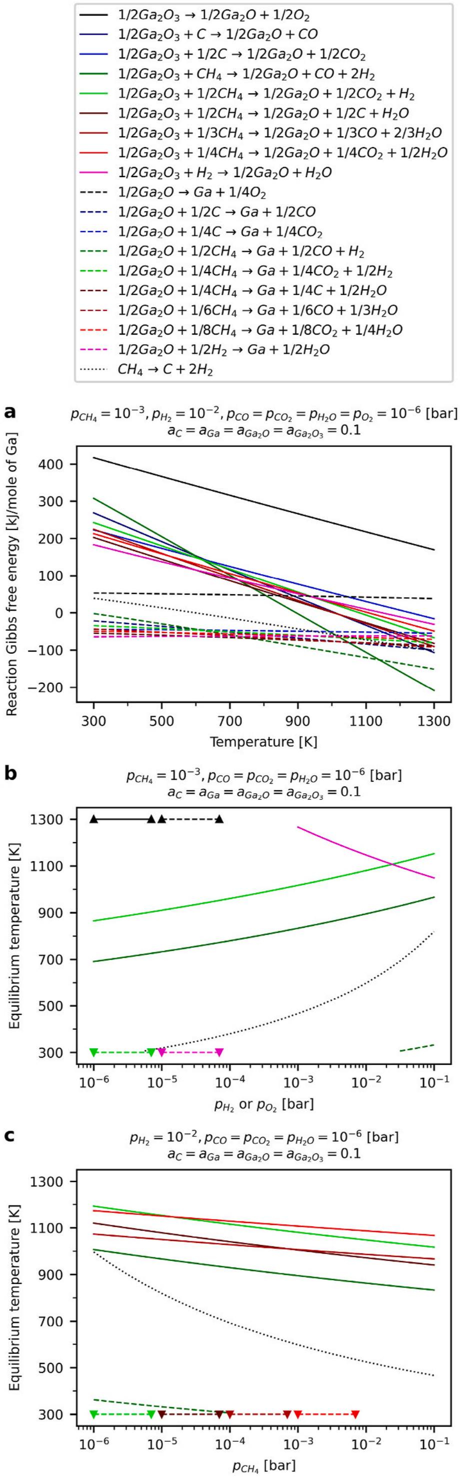

Fig. 1. Thermodynamic properties of reactions involved in gallium oxide reduction in the 300–1300 K range. a) Calculated reaction Gibbs free energies of the indicated reactions as a function of temperature. The indicated values for gas partial pressures and condensed-phase activities are selected such to roughly match their order of magnitude values in the reported CVD experiments. The reaction equilibrium temperatures can be extracted from the zero reaction free energy values. b) and c) The equilibrium temperatures of reactions involving O_2, H_2, and CH_4 gases as a function of their partial pressures. For the lines that lay out of the plotted temperature range, the triangular markers point whether they lay above or below the range.

temperatures for gallium oxide reduction corresponding to the implemented range of gas partial pressures are indicated in the T_{red} columns. For the annealing stage T_{red} corresponds to the reduction of Ga_2O_3 by hydrogen (solid magenta line in Fig. 1), and for the growth stage it corresponds to the reduction of Ga_2O_3 by methane via CO and H_2 formation (solid dark green line in Fig. 1). Only Wang et al. [8] and Zhu et al. [23] have reported an annealing stage capable of removing the gallium oxide (*i.e.* $T > T_{\mathrm{red}}$), if their annealing time has been long enough to allow complete reduction. For the other reports, an oxide overlayer must have been present on the liquid phase at the beginning of the graphene growth stages. In these cases, methane dissociation has happened (at least initially) on the solid gallium oxide skin rather than on liquid metallic gallium.

During the graphene growth stage at high enough temperatures, the methane content of the feedstock can gradually reduce the gallium oxide skin. As mentioned, the H_2 content of the CVD gas and the deposited carbon can also reduce the gallium oxide in parallel, however, their contributions are expected to be secondary in comparison to methane. For the feedstock compositions of the growth stage indicated in Table 1, our calculated equilibrium temperatures for Ga_2O_3 reduction by CH_4 (leading to CO and H_2 formation) are indicated in the last T_{red} column. It is found that the growth recipes of Ding et al. [7], Wang et al. [8], Hiyama et al. [12], and Zhu et al. [23] are capable of removing the gallium oxide overlayer, if the exposure time to CH_4 has been long enough to complete the reduction. In order to know if the annealing or growth durations were long enough to remove the gallium oxide layer, one needs to investigate the kinetics of the reduction process, which is beyond the scope of this comment. To our knowledge, Zhu et al. are the only group who have used *ex situ* Raman spectroscopy to check whether a remnant gallium oxide is present below the overgrown graphene layer or not [23]. Consistent to the results of our analysis, they found no evidence of such underlying oxide layer.

Meanwhile, our thermodynamic calculation indicates that the low-temperature growth recipe of Fujita et al. is not capable of reducing the gallium oxide, regardless of the CVD duration [13]. In this case, we expect that the stronger catalytic activity of gallium trioxide (Ga^{3+}) has been responsible for successful graphene CVD growth at such low temperatures, and graphene has actually grown in the presence of a solid Ga_2O_3 skin throughout the experiment.

4. Conclusion

Our presented thermodynamic analysis indicates that during several of the previously reported experiments of graphene CVD growth on liquid gallium, an atomically thin gallium oxide layer should have covered the liquid gallium. This means that graphene have actually grown on the solid oxide skin rather than on the liquid metal. These insights point towards a more complex mechanism of graphene growth on liquid gallium than considered before. Meanwhile, the presence of a solid oxide skin on the liquid substrate should not necessarily be regarded as a problem, as its distinct rheological and catalytic effects, and the possibility of using it as a sacrificial layer during CVD, can provide new mechanisms and opportunities for 2D materials synthesis.

Author contributions

MS initiated the H2020 and INIC projects, conceived this study, performed the thermodynamic calculations, and wrote the paper. SMM has contributed to the paper and supervised the INIC project. IG has contributed to the paper, supervised and coordinated the H2020 projects.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

Table 1
The recipes used in the literature for graphene CVD on liquid gallium, ordered by their publication date. The indicated parameters include total pressure (P_{tot}), flow rates of the feedstock gases (sccm), and temperature (T). For the annealing and growth stages, the predicted equilibrium temperatures for gallium oxide reduction are shown in the corresponding T_{red} columns.

		Annealing				Growth				
Ref.	P_{tot} [bar]	Ar [sccm]	H_2 [sccm]	T [K]	T_{red} [K]	Ar [sccm]	H_2 [sccm]	CH_4 [sccm]	T [K]	T_{red} [K]
[7]	1.0	NA	NA	NA	NA	200	0–100	5	1273	664–959
[8]	1.0	300	0–30	1293	1052–1869	300	0–30	5–20	1293	658–919
[23]	1.0	200	2	1273	1146	200	0	1.5	1273	674
[12]	0.5	NA	NA	NA	NA	250	0	0.05	773	692
[13]	2.0×10^{-4}	NA	NA	NA	NA	250	0	0.05	573	580

the work reported in this paper.

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