

**Temperature Study of CVD Graphene on Cu Thin Films:
Competition between C Catalysis and Cu Dewetting**

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Temperature study of CVD graphene on Cu thin films: competition between C catalysis and Cu dewetting

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ABSTRACT

In this paper we report on a systematic study of the Cu thin film dewetting by the monitoring of the intensity of the infra-red emission from the film surface during Rapid Thermal Chemical Vapor Deposition of graphene. The time evolution of Cu coverage highlights three typical stages of dewetting which strongly depend not only on the temperature and film thickness, but also on the pressure and composition of the gas in chamber. Consequently, we demonstrate that the Cu surface can be effectively activated in films at temperatures lower than in foils and the process can be fully controlled by adjusting those parameters, in order to reach the optimal conditions for graphene growth.

INTRODUCTION

Chemical Vapor Deposition (CVD) is one of the most promising techniques for large area graphene production. The configuration that up to this time has been more studied is CVD on Cu foils used as catalyst. On the other hand deposition of graphene onto Cu films could give many advantages related to the compatibility with current microelectronics technology, furthermore evaporated metals present less contaminations and there is much less copper to dissolve during transfer.

However the main drawback of the synthesis of graphene on copper thin film is the dewetting of the substrate occurring at high temperature. This phenomenon is driven by surface energy minimization and can occur via surface diffusion under film's melting temperature and consists in the agglomeration of the film forming holes and eventually islands. Dealing with polycrystalline thin films, dynamics is well studied [1][2] and consists in three different stages: hole formation, propagation and ligament breakup. The phenomenon occurs at the boundaries of three or more grains and evolves in time through the retracting of grains and the deepening of the grooves. The stage before hole opening can be defined as incubation stage.

Such dynamics of the surface can be seen as a problem for a good CVD, so in order to increase the incubation time, what is usually done is to increase the thickness of the film (>500nm) [3]–[5] approaching to the properties of the foil. On the other hand dewetting has also been proposed as a resource for a direct deposition of graphene on the substrate (usually SiO₂) below copper [6].

However, CVD of graphene is still not fully understood, but the condition, considered essential for a better catalysis, is the high mobility of the Cu surface atoms with behavior close to a liquid [7].

Here we report a study of the substrate dewetting and a possible approach to increase the controllability and reproducibility of the CVD deposition process of graphene on Cu thin (<500nm) films.

EXPERIMENTAL

The dewetting study has been performed on Cu films with thicknesses of 200 and 350 nm. Depositions have been performed by using an electron beam evaporator on SiO₂ (285 nm)/Si substrates at 0.17 nm/s in the 10⁻⁷ mbar range.

Graphene deposition has been carried out in a Jipelec JetFirst 100C Rapid Thermal CVD (RTCVD). This system allows heating and cooling at high rates (tens °C/s), making the interpretation of the dewetting dynamics simpler than in a conventional resistive furnace. Heating is provided by halogen lamps on the top of the chamber and the sample placed horizontally onto three quarts. For the aim of this work, the sample is mounted upside down exposing Cu covered surface directly to the pyrometer; the temperature is measured by a thermocouple contacting the sample's back face. The pyrometer mounted in our RTCVD system measures the infrared emission of the heated sample at a centered wavelength of $\lambda=5.14 \mu\text{m}$. The signal of the pyrometer is proportional to the Planck's black body radiation law and to the body emissivity (ϵ). Since the emissivity of the film (ϵ_{Cu}) is lower than the emissivity of the substrate (ϵ_{SiO_2}), we are able to monitor the dewetting process as a gradual transition from ϵ_{Cu} to ϵ_{SiO_2} due to the progressive Cu agglomeration.

Several trials have been done in low vacuum conditions (approx. 10⁻² mbar) with temperatures ranging from 600°C to 900°C. Fig. 1 shows the evolution of the pyrometer signal at different temperatures. Focusing on the 600°C curve, after a first signal rise due to sample heating, the incubation stage of dewetting is observed as a constant signal value for a time interval t_0 . For higher temperatures the behavior is similar, but t_0 lowers. At 900°C the incubation time is no more measurable since dewetting occurs already during the heating ramp.

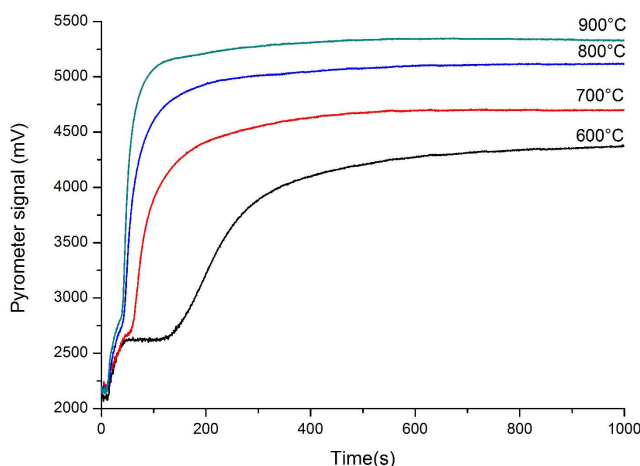


Fig. 1 Pyrometer signal acquired at different temperatures for 200 nm Cu films.

Table I summarizes the incubation times for both the samples of 200nm and 350nm in vacuum conditions at different temperatures. At fixed temperature the incubation time increases at least one order of magnitude accordingly with the sample thickness. Such behavior justifies the common use of thicker films to prevent dewetting.

Table I Incubation time for Cu 200nm thick (in Vacuum and hydrogen environment) and 350 nm thick.

t_0	600°C	700°C	800°C	900°C
200 nm Vacuum	100s	12s	1s	-
200 nm H₂	980s	410s	14s	-
350 nm Vacuum	1000s	420s	180s	53s

Figure 2 shows four SEM micrographs of the 350 nm Cu thin film at different stages of dewetting at 700 °C. In particular, in a) bumped grains are already visible just after the heating ramp. After 400 s, holes start to grow (b) and become large with time. It is worth noticing that during the incubation time the copper mobility is already enhanced suggesting that a dynamic surface, close to being a liquid, is attainable in films at temperatures lower than in case of foils ($T > 1000$ °C). In fact, when using Cu foils, such high temperatures seem to be necessary also if C precursor catalyzes at lower temperatures [8].

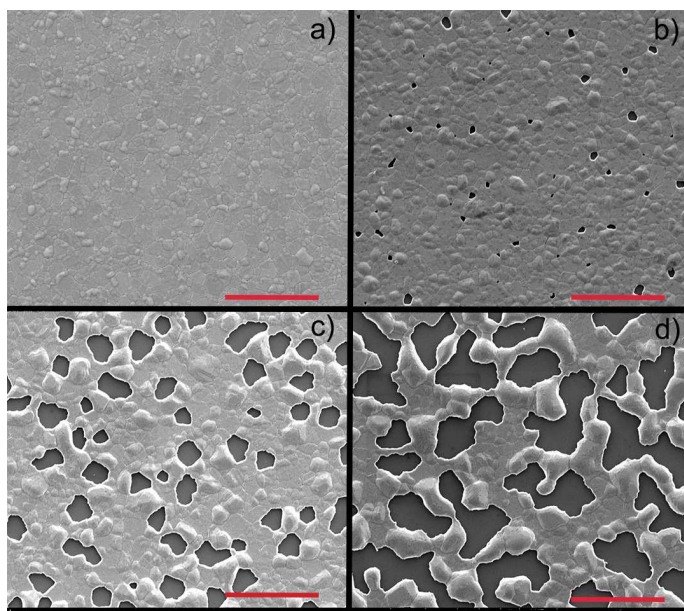


Fig. 2 Cu thin film 350 nm during four stages of dewetting at 700 °C. a) after heating; b) after 400 s; c) after 1200 s; d) after 3000 s. Scale bars are 10 μ m.

In addition to thickness and temperature, another tunable parameter in CVD is the pressure. Apart from the precursor gas, many authors employ H₂ to reduce the Cu oxide and activate the catalyst surface prior to graphene deposition. In order to analyze the role of H₂, solely, we performed the same process that was done in vacuum in H₂ environment at 0.25 mbar pressure on samples with 200 nm Cu. t_0 values (summarized in table 1) approach to those of the thicker

films for temperature of 600 °C and 700 °C while they dramatically drop for higher temperatures.

When exposing the 200 nm thick Cu sample at 0.25 mbar of Ar, the dynamics is much slower with $t_0 > 1500$ s suggesting a major role played by the mass of the gas atoms on the dewetting process.

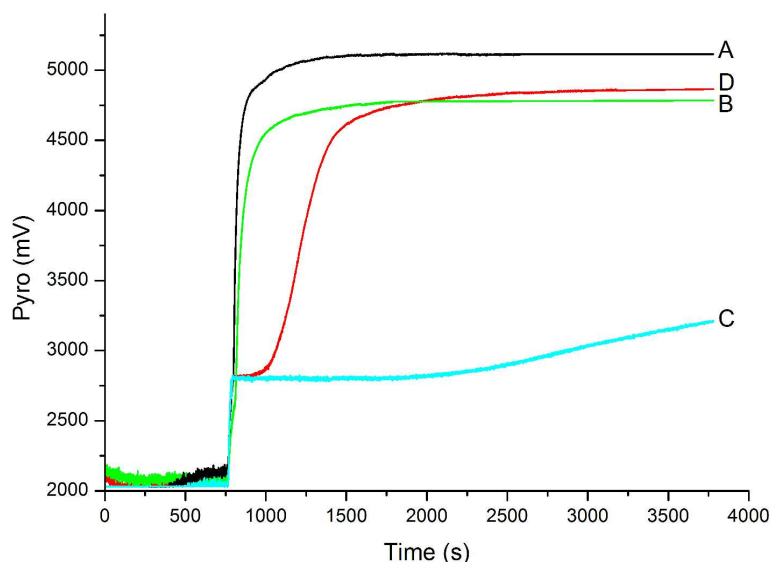


Fig. 3 Comparison of the pyrometer signal at 800 °C: the curve A is related to a 200 nm thick film in vacuum (10^{-2} mbar), B to a 200 nm thick film in hydrogen environment (0.25 mbar) and C to a 200 nm thick film in argon environment (0.25 mbar). The curve D refers to a 350 nm thick film in vacuum (10^{-2} mbar).

With the aim of studying the possibility of activating the Cu surface, reducing the Cu oxide [9] and preserving the dewetting at the same time, we prepared a recipe in which a Ar/H₂ mixture (10:1 flux ratio) is fluxed for 6 min keeping pressure at 0.25 mbar. Instead of the more commonly used methane, which is dissociated at higher T, we used ethanol [8], [10], [11] at T=700 °C. It is worth noting that, when ethanol vapors are fluxed, no emissivity-related rise in the pyrometer response is detected in the deposition time window, i.e. dewetting does not occur during deposition for times up to 1500 s. During the cooling stage Ar is fluxed again in the chamber to preserve the Cu film underneath.

It is important to note that neither the pre-deposition nor the deposition steps are optimized. As previously discussed, the aim of this work is to identify the possibility of controlling dewetting in the catalysing film, in order to obtain a dynamic surface, necessary for better graphene deposition, avoiding the film rupture at the same time. To achieve optimal results, several parameters have to be finely adjusted, namely, film thickness, temperature, pressure chamber, and gas composition and fluxes in both pre-deposition and deposition steps. As an example, no H₂ is added to hydrocarbon source during deposition, as it has been proved that small amounts of H₂ can be beneficial to the graphene quality[8]. In the deposition chamber a Cu foil has been added in order to evidence differences between the two systems.

Raman mapping of graphene obtained in this way indicates a uniform mono/bi-layer has been obtained, as suggested by the intensity ratio of 2D and G peaks (Fig. 4). It is important to note that the same deposition conditions yield much higher quality graphene on Cu films rather than on foils. In this case, in fact, the Raman spectrum is indicative for a nanocrystalline multilayered graphene film[12]. This confirms that, in the investigated T range, a dynamic,

quasi-liquid Cu surface is achievable only in films, and can be controlled by different pre-deposition conditions.

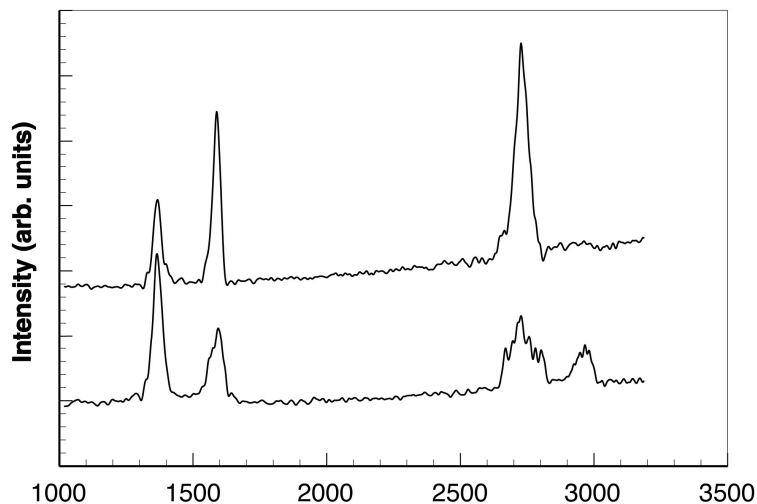


Fig. 4 Raman spectra of graphene deposited on Cu at 700 °C. . The upper one refers to the process on Cu film, the lower on Cu foil. To avoid background luminescence from Cu, illumination at 442 nm has been employed [5].

CONCLUSIONS

In conclusion, we have developed a simple and effective method to monitor the dewetting process of catalyst film before and during graphene deposition. The pre-deposition stage reveals very important to activate the catalyst surface. By controlling the pressure in the chamber by addition of gaseous molecules it is then possible to increase the Cu atoms mobility in order to have a quasi-liquid surface, inhibiting hole opening and film agglomeration. Finally, we have demonstrated that such quasi-liquid surface is obtainable in films at temperatures lower than in Cu foils. This opens the possibility of producing high quality graphene on Cu films at low temperatures.

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