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In situ control of dewetting of Cu thin films in graphene chemical vapor deposition

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ABSTRACT

Chemical vapor deposition (CVD) on Cu thin films is a promising approach for the large area formation of graphene on dielectric substrates, but a fine control of the deposition parameters is required to avoid dewetting of the Cu catalyst. In this paper we report on the study of the Cu dewetting phenomena by monitoring the intensity of the infra-red emission from the film surface during rapid thermal CVD of graphene. The reduction of Cu film coverage consequent to dewetting is detected as a variation of sample's emissivity. Results indicate three time constants of dewetting, describing three typical stages, hole formation, propagation and ligament breakup. Slowing the first incubation stage by tuning pressure in the chamber allows for an effective surface activation resulting in the deposition of graphene at temperatures lower than those in the case of Cu foils.

1. Introduction

Compared to the wealth of information available in current literature about the CVD (chemical vapor deposition) of graphene onto Cu foils [1], there is a dearth of experimental studies dealing with the use of Cu thin (<500 nm) films as substrates [2–5]. However, these latter offer several advantages: first, they are deposited in high vacuum environments and show less contamination than commercial foils, second, the small amount of the Cu substrate makes the graphene transfer process much less invasive, and third, the use of films makes the process more compatible with the current microelectronics technology.

One of the most critical factors which hinder the adoption of Cu thin films as substrates for CVD deposition of graphene is their metastability of the films, since they undergo agglomeration (more commonly defined as dewetting) if treated at high temperatures. Such effect is well known from several decades [6], and theoretically studied since the 1970s. Dewetting is known to appear in films with different crystallographic quality, no matter if mono-crystalline [7] or poly-crystalline [8]. In the latter case, a simple model based on the balance of the surface tension [8] at a grain boundary can be drawn. The equilibrium between the grain boundary (GB) energy γ_{GB} and the surface energy γ_s allows defining the angle φ, which determines the curvature of the grain surface as [9]:

$$\varphi = \sin^{-1}\left(\frac{\gamma_{GB}}{2\cdot\gamma_s}\right), \tag{1}$$

and calculations lead to obtain the depth δ of the forming groove at the GB as:

$$\delta = \frac{R\cdot\left(2-3\cdot\cos\varphi+\cos^3\varphi\right)}{3\cdot\sin^3\varphi} \tag{2}$$

where R is the average radius of the grain. When δ equals the film thickness h_0, a hole is formed in the film. The stage prior to hole opening is defined as the incubation stage.

When using thin films of metal catalyst (e.g. Cu) for graphene CVD, researchers tend to increase the hole incubation time (t_0), generally by using thick films [10–15] (≥500 nm). As a matter of fact, thicker Cu films can be simply treated as foils, then applied with the same deposition conditions, with comparable results [10]. Nevertheless, deep grooves at GBs are likely formed and the graphene sheet may pucker in some regions when transferred, as elucidated by the AFM (atomic force microscope) image in Fig. 1. Such puckering is not to be confused with wrinkles due to the difference in thermal expansion between the graphene and the substrate [8], because it is observed on the transfer destination substrate, solely [16].

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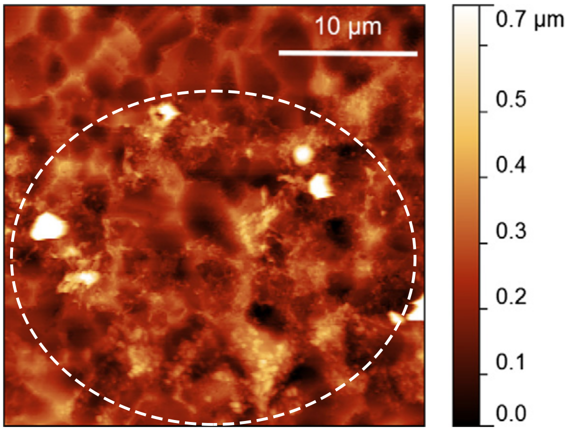

Fig. 1. AFM image of a graphene sheet transferred onto PMMA. Due to its viscosity, PMMA does not fill the deep grooves when spun onto the film. Graphene, which follows the Cu film corrugations, is puckered in those regions after transfer (circled areas).

However, film dewetting should not merely be considered as an obstacle, but as an additional resource to open alternative chances for the large scale graphene synthesis. For example, the possibility of carefully laying down the graphene sheet onto the substrate underlying the Cu film (typically SiO_2), just during deposition, avoids cumbersome and time consuming transfer processes [4]. In addition, in a film subjected to dewetting, the surface is close to being liquid. This is considered as necessary for optimal graphene growth on Cu [1].

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

2. Experimental

Cu films of 200 nm and 350 nm, evaporated at a rate of 0.17 nm/s onto oxidized Si substrates at pressures in the 10^{-5} Pa range have been employed for the purpose. Substrates have been cleaned in a class 100 clean room by sonication in acetone and isopropanol, then rinsed in deionized water, dried in N_2 flow and rapidly loaded into the evaporator chamber. Just after Cu evaporation the specimen has been transferred into a Jipelec JetFirst 100 rapid thermal CVD (RTCVD) system, and promptly evacuated down to the 10^{-3} Pa range to minimize oxidation due to air exposure. The RTCVD apparatus allows heating and cooling at high rates (tens of °C/s), making the interpretation of dewetting dynamics simpler that in a conventional resistively heated furnace. In the RTCVD system, a wafer is placed horizontally onto three quartz pins and heated by means of an array of halogen lamps on the top of the chamber.

For the aim of this work, the sample is mounted upside down in the chamber (see Fig. 2) and its temperature is measured by three thermocouples in contact with the sample back face.

A quartz window allowed thermal radiation emission from the Cu layer to be monitored by means of a pyrometer with a centered wavelength of $\lambda = 5.14$ μm (Fig. 2).

Being the signal of the pyrometer proportional to the Planck's black body radiation law and to the body emissivity (ε) and since the emissivity of the film (ε_{Cu}) is approximately 2 times lower that the emissivity of the substrate (ε_{SiO_2}), we expect to monitor the dewetting process as a gradual transition from ε_{Cu} to ε_{SiO_2}:

$$\varepsilon_{eff}(t) = \varepsilon_{Cu} \cdot x(t) + \varepsilon_{SiO_2}[1-x(t)] \rightarrow B(t) = B_{Cu} \cdot x(t) + B_{SiO_2}[1-x(t)]. \quad (3)$$

Where ε_{eff} is the effective emissivity of the partially covered SiO_2 surface (film experiencing dewetting) and $x(t)$ is the percentage of the surface covered with Cu, which decreases with time; correspondingly, on the right side, $B(t)$ is the relevant signal of the pyrometer at time t

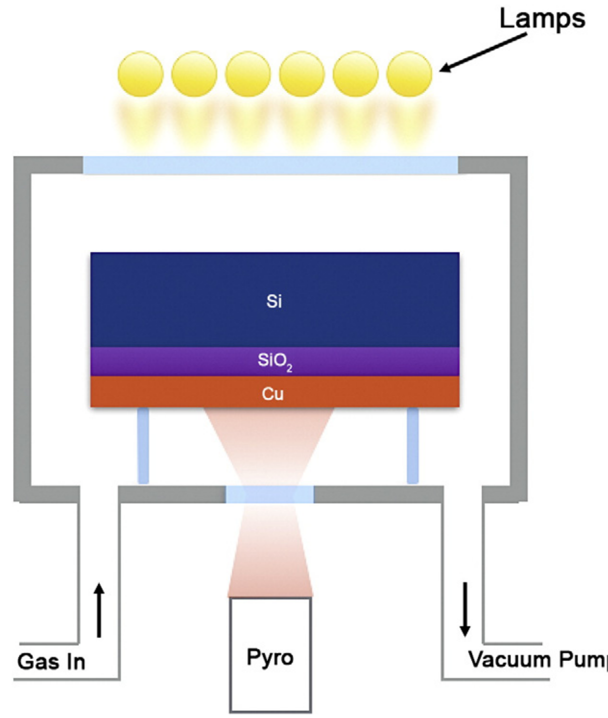

Fig. 2. Scheme of the RTCVD system.

and B_{SiO_2} and B_{Cu} are the signals measured from pure SiO_2 and Cu samples, respectively.

We measured the final relative Cu coverage x_{SEM} by analyzing the SEM (scanning electron microscope) micrographs of the dewetted samples using the ImageJ software [17]. Markers on the right side of Fig. 3

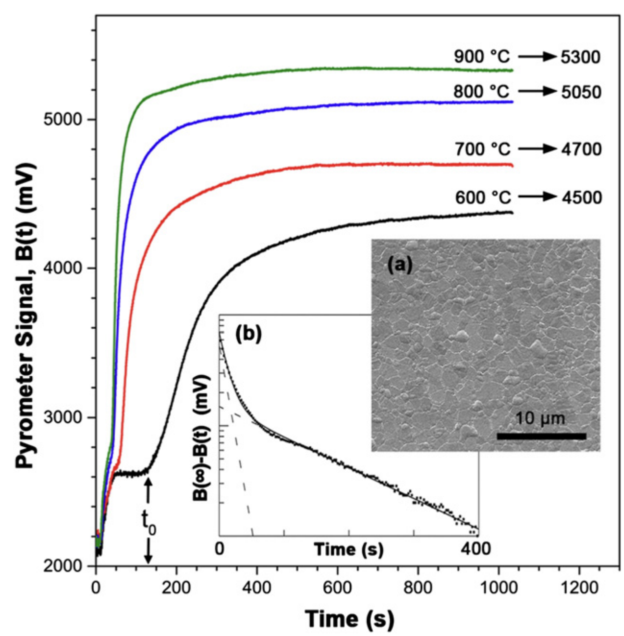

Fig. 3. A collection of pyrometer responses B(t) taken on a 200 nm thick Cu film dewetted in vacuum at different temperatures. B(∞) is the response value at saturation. Initial rise corresponds to the heating ramp, whereas the second one is related to the change in emissivity due to hole opening and coalescence in the Cu film. The incubation stage is clearly visible in between the two rises for the curves at lower temperatures. Arrows on the right indicate B values, as evaluated by inserting in Eq. (3) the final surface coverage by software analysis on SEM micrographs. Inset (a): surface topography of a Cu film extracted just after heating up to 700 °C, showing the presence of surface bumps. Inset (b): the complementary curve of the emissivity-related rise at 800 °C displayed in the main graph: a satisfactory fit (full line) is obtained by using a double exponential function (dashed lines).