



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



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ARTICLE INFO

Article history:

Received 10 March 2014

Received in revised form 21 October 2014

Accepted 29 October 2014

Available online 5 November 2014

Keywords:

Dewetting

CVD graphene synthesis

Structural transformation

Chemical vapor deposition

Infra-red emission

Electron microscopy

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.

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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]:

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

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

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

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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