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Nanomechanical mapping of graphene layers and interfaces in suspended graphene nanostructures grown via carbon diffusion

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ABSTRACT

Graphene's remarkable mechanical, electronic and thermal properties are strongly determined by both the mechanism of its growth and its interaction with the underlying substrate. Evidently, in order to explore the fundamentals of these mechanisms, efficient nanoscale methods that enable observation of features hidden underneath the immediate surface are needed. In this paper we use nanomechanical mapping via ultrasonic force microscopy that employs MHz frequency range ultrasonic vibrations and allows the observation of surface composition and subsurface interfaces with nanoscale resolution, to elucidate the morphology of few layer graphene (FLG) films produced via a recently reported method of carbon diffusion growth (CDG) on platinum-metal based substrate. CDG is known to result in FLG suspended over large areas, which could be of high importance for graphene transfer and applications where a standalone graphene film is required. This study directly reveals the detailed mechanism of CDG three-dimensional growth and FLG film detachment, directly linking the level of graphene decoupling with variations of the substrate temperature during the annealing phase of growth. We also show that graphene initially and preferentially decouples at the substrate grain boundaries, likely due to its negative expansion coefficient at cooling, forming characteristic "nano-domes" at the intersections of the grain boundaries. Furthermore, quantitative nanomechanical mapping of flexural stiffness of suspended FLG "nano-domes" using kHz frequency range force modulation microscopy uncovers the progression of "nano-dome" stiffness from single to bi-modal distribution as CDG growth progresses, suggesting growth instability at advanced CDG stages.

1. Introduction

Graphene is a remarkable material which has not only paved the way for the investigation of fundamental material properties [1] but has also given credence to the prospect of devices for energy storage and generation [2], displays [3] and transparent flexible heaters [4]. For all these applications the interaction of the graphene layer with the underlying substrate plays a key role, by defining the quality of graphene transfer and hence influencing device application performance. It may also be highly desirable to isolate the graphene layer from the substrate through suspended regions, a time and material intensive process with typical layers grown via chemical vapour deposition (CVD) [5]. Towards this goal, it has been shown that few layer graphene (FLG) films fabricated via the recently reported method of carbon diffusion growth (CDG) on platinum-based metal become effectively decoupled from the substrate resulting in μm sized areas of suspended FLG films [6]. Such detachment of graphene from the growth substrate can play a significant role in facilitating graphene transfer that is crucial for practical applications such as displays and lighting [7] or where suspended films are required for nanoscale switches, microelectromechanical systems or sensors [8–10].

At the same time, neither the detailed aspects of graphene–substrate interaction in CDG graphene, nor the mechanism of the initiation of film suspension has been elucidated so far. As nanoscale features of graphene–substrate interfaces are hidden under the immediate graphene surface and can be often masked by the pre-existing substrate topography, innovative solutions are required to explore these layered nanostructures. In this work we complement traditional scanning electron microscopy, atomic force microscopy (AFM) and Raman studies of FLG films [11,12], with nanomechanical mapping using ultrasonic force microscopy (UFM) [13]. UFM is known for its material sensitive imaging of surface, interfacial and subsurface [14,15] features of solid state materials including graphene layers [16]. It allowed us to explore the mechanism of decoupling FLG regions and the three dimensional mechanism of CDG graphene growth. The local properties of decoupled FLG films were further examined using quantitative stiffness mapping using kHz frequency range force modulation microscopy (FMM) which allowed exploration of these properties for different stages of the CDG process. The approach to mapping nanomechanics of thin films and film–substrate interactions developed and refined over the course of this work

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allows the studies of growth and functioning of a wide diversity of films and layered materials.

2. Experimental details

2.1. CDG of graphene film on Pt substrates

FLG films were synthesised on an 8-inch Si(100) wafer via the so-called CDG, or segregation method [6]. The procedure was as follows: i) first, the Si(100) wafer was thermally oxidized at 1050 °C to form a 300 nm-thick SiO_2 film; ii) the amorphous silicon carbide (a:SiC:H) was then deposited at 250 °C temperature and ca. 270 Pa pressure on the wafer inside a commercially available chamber (CENT 5200, Applied Materials, USA) using radio frequency (RF) plasma CVD with a frequency of 13.56 MHz and a power of 400 W in a capacitive coupled parallel plate system; the plasma composition consisted of 200 standard cubic centimetres per minute (sccm) propene, 500 sccm trimethylsilane and 1000 sccm He plasma mixtures; and iii) followed by 50 to 200 nm Pt deposited on the top of a:SiC:H at room temperature by physical vapour deposition using a commercial Pt target of 99.999% purity. This process resulted in a Pt/a:SiC:H/SiO2/Si(100) sandwich structure that was finally annealed in an integrated annealing furnace (Metal Anneal Chamber, Applied Materials, USA — chamber diameter and length were, correspondingly, 120 and 300 mm) leading to the formation of Pt_3Si layer, diffusion of carbon to the surface and graphene growth [6]. The temperature of the substrate, during this annealing phase, can be varied and is typically between 600 °C and 850 °C. In the present experiment, the wafer has been annealed at average 800 °C for 15 min, with inhomogeneity at temperature of up to ca. 50 °C across the wafer.

Morphologically, we found that graphene film formed via CDG growth exhibits three distinctive morphologies across a single wafer linked to the substrate temperature variation during annealing, so that the central area is about 50 °C hotter than the wafer perimeter. These stages correspond to the primary conformal growth (lowest temperature) where graphene seems to be uniformly covering a flat surface of Pt/Pt_3Si exhibiting sub-μm grain structure (marked as **P** (primary) in Fig. 1(a)); secondary stage, grown at the intermediate temperature, corresponding to graphene on almost flat Pt/Pt_3Si showing some topographical variations of protruding and dimpled areas (**S**, Fig. 1(b)); and a tertiary stage in the centre of the wafer grown at temperatures higher than that in the primary stage by approximately of 50 °C where scanning electron microscopy (SEM) images show a much rougher structure (**T**, Fig. 1 (c)) with different SEM contrast of elongated interconnected islands and large areas of graphene, the latter suspended between islands of Pt/Pt_3Si consistent with results previously reported [6]. The SEM images were taken with a S5500 microscope purchased from Hitachi, Japan, in secondary electron mode with an emission voltage and a current of 30 kV and 20 μA, respectively. Tertiary regions can be easily identified by low magnification optical microscopy or even with the naked eye due to varying optical reflectance.

Fig. 1(d) shows Raman spectrum of the freshly grown sample, measured on the centre of the wafer, on the tertiary (**T**) region, using 488 nm laser of spot size 1–2 μm of 7.9 mV (LabRAM, Horiba — Jobin Yvon). The Raman spectra were similar whether taken either on the protruding islands or on the suspended graphene [6]. Estimation of graphene thickness, based on the theory of Reina et al. [17] using the

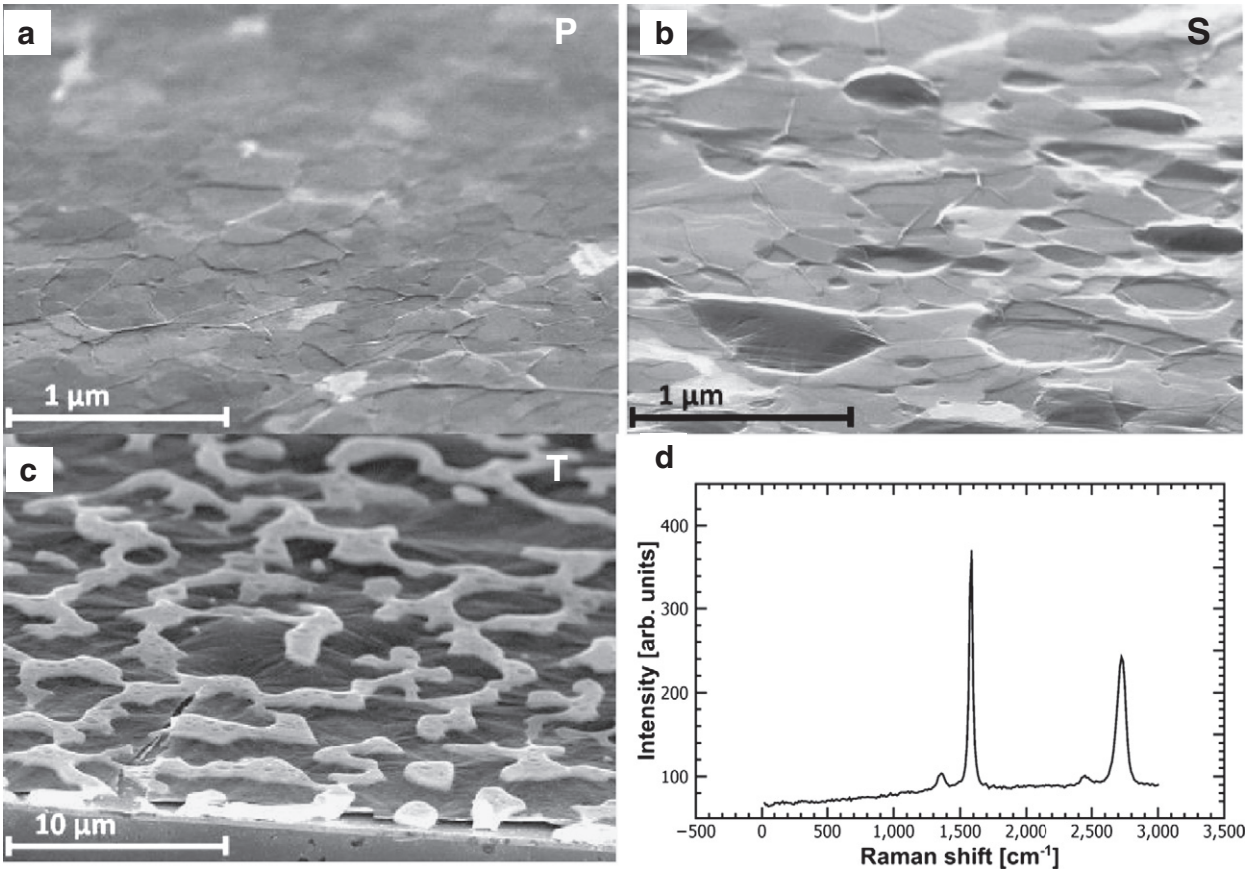

Fig. 1. Characterisation of graphene layers prepared via CDG on Pt-based metal substrate. SEM images of (a) the primary (marked as **P**), (b) secondary (**S**) and (c) tertiary (**T**) stages of growth progression linked with the increase of annealing temperature. (d) Raman spectrum of graphene film; spectra were found to be independent of growth site and stage.