



## New synthesis method for the growth of epitaxial graphene

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### ABSTRACT

As a viable candidate for an all-carbon post-CMOS electronics revolution, epitaxial graphene has attracted significant attention. To realize its application potential, reliable methods for fabricating large-area single-crystalline graphene domains are required. A new way to synthesize high quality epitaxial graphene, namely “*face-to-face*” method, has been reported in this paper. The structure and morphologies of the samples are characterized by low-energy electron diffraction, atomic force microscopy, angle-resolved photoemission spectroscopy and Raman spectroscopy. The grown samples show better quality and larger length scales than samples grown through conventional thermal desorption. Moreover, the graphene thickness can be easily controlled by changing annealing temperature.

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### 1. Introduction

Graphene, a two-dimensional array of carbon atoms in honeycomb lattice, has been theoretically studied for decades in terms of the fundamental building block of carbon based materials, such as graphite and carbon nanotubes [1,2]. However, the first observation of freestanding graphene was not realized until 2004 with mechanical exfoliation method by peeling graphene flakes from a bulk graphite crystal onto SiO<sub>2</sub> substrate [3]. Since then, a variety of novel properties, including quantum Hall effects, and relativistic quasiparticles with a group velocity of  $1/300c$  (where  $c$  is the speed of light) [4–6] have been observed. These unique properties, together with the high values of conductance, mobility, and mechanical strength [4,7,8] make graphene a promising material for a wide variety of new technological applications [9–11], such as post-CMOS digital electronics, single-molecule gas sensors, and spintronic devices.

To realize the application potential of graphene, reliable methods for fabricating large-area single-crystalline graphene domains are required. The most promising approach in this respect seems to be the controlled graphitization of SiC surfaces [9,12]. In this

method, single layer and/or multilayer graphene can be grown by sublimating Si atoms from SiC substrates at high temperature. In spite of a lot of efforts devoted to the improvement of synthesis methods to form large areas of uniform, electronic grade graphene by the thermal desorption process is still very challenging. In this paper, we will give a short review on the current state of epitaxial graphene research, and we will then introduce a new developed synthesis method, the “*face-to-face*” method, which allows preparing good quality monolayer, bilayer and three layer epitaxial graphene samples on 6H-SiC(0001) substrate.

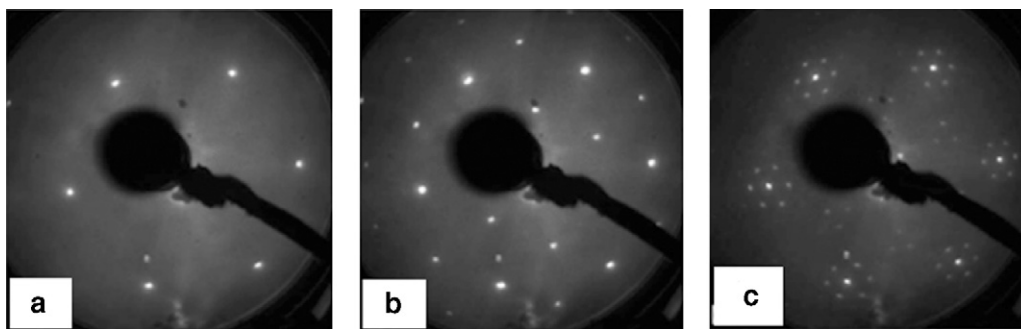
Although the epitaxial growth of graphene on semiconducting substrates was known as early as 1975 [13], renewed interest in this field over the past few years is certainly due to: the discovery of the fractional quantum Hall effect in freestanding graphene, the observation of 2D electron gas behavior also in the epitaxial samples [9] as well as the appealing possibility to incorporate the existing silicontechnology to mass produce and pattern epitaxial graphene.

As of today, a variety of different methods have been developed to grow graphene epitaxially, both on semiconducting and on metallic substrates that have good lattice matching with graphene. All these different methods can be classified into three categories: (a) thermal decomposition of carbide (particularly SiC); (b) cracking of hydrocarbon gas on other carbide substrates (TiC, TaC, WC, etc.) and metallic substrates (Ni, Pt); (c) segregation of the carbon atoms from the bulk (Ru(001)).

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**Fig. 1.** LEED patterns with a primary energy of 180 eV, obtained at four different stages during the growth of sample A. (a)  $1 \times 1$  spots of SiC, after a 5 min anneal around  $1000^\circ\text{C}$  followed by the initial cleaning procedure under Si flux. (b)  $(\sqrt{3} \times \sqrt{3})R30$  reconstruction, after 5 min around  $1100^\circ\text{C}$ . (c)  $(6\sqrt{3} \times 6\sqrt{3})R30$  reconstruction, after 10 min around  $1250^\circ\text{C}$ .

In this paper we will focus on the epitaxial growth of graphene on SiC substrate, being this most relevant to our newly developed method.

## 2. Epitaxial graphene on SiC

Although growing thick graphite samples on SiC has been a well-known process for many years [13–15], it is not until recently that the thickness was pushed down to few layers and a full characterization of the high quality graphene sample has been carried out [9,16,17]. The growth of epitaxial graphene on SiC is based on thermal decomposition of the SiC substrate. Both e-beam heating and resistive heating have been used, but no difference seems to arise from the different heating methods [18]. In order to avoid contaminations the heating is usually performed in ultra-high vacuum (UHV) environment. Similar results have been observed for high and/or low base pressure growth but so far no comparative study about the influence of the background pressure in the vacuum chamber has been conducted. From the molar densities one can calculate that approximately three bilayers of SiC are necessary to set free enough carbon atoms for the formation of one graphene layer [18]. The growth of graphene can take place on both the  $(0001)$  (silicon-terminated) and the  $(00\bar{0}1)$  (carbon-terminated) faces of 4H-SiC and 6H-SiC wafers. The main difference lies in the sample thickness that one can achieve. In the case of silicon face, the growth is slow and terminates after relatively short time at high temperatures giving rise to very thin samples, up to a monolayer. On the contrary, in the case of the carbon face, the growth does not self-terminate giving rise to relatively thick samples (approximately 5 up to 100 layers) [19] with larger orientational and turbostatic disorder [20–22].

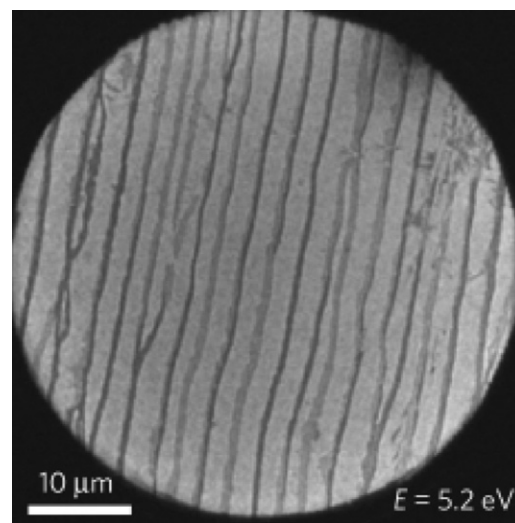
Below we will briefly review the growth conditions for epitaxial graphene on SiC substrate. For a detailed review see [19].

## 3. Epitaxial graphene on SiC(0001) face

Hydrogen etching is performed as a normal routine of pretreatment to remove scratches from polishing and oxides and leave a surface with highly uniform, atomically flat terraces. Although it is believed that larger graphene sheets should be obtained with a smoother graphitization surface [23], the relevance of pre-graphitization SiC surface to better graphene order has not been substantiated. Recently, the relation between initial surface morphology and sample quality has been discussed by Ohta et al. [24]. They observed the formation of graphene on SiC by Si sublimation in Ar atmosphere, and identified two types of monolayer graphene with different shapes. It was noticed that large graphene sheets preferred to grow along the triple bilayer SiC steps, while narrow graphene ribbons formed following the surface of single bilayer

SiC height. The dependence between growth mechanisms and initial surface morphology indicates the effects of  $\text{H}_2$  etching on the formation of graphene. The result suggests that by minimizing the number of single bilayer SiC steps with  $\text{H}_2$  etching, better graphene sample should be achieved.

To compensate the depletion of Si during the pre-cleaning process, external Si flux is applied before the SiC substrate is heated to higher temperature to grow graphene. A number of surface reconstructions prior to graphitization have been observed and studied by low-energy electron diffraction (LEED) [14,16]. Fig. 1 shows LEED patterns obtained at different stages during the growth of graphene. The initial Si-rich  $(3 \times 3)$  phase can be obtained by exposing a well-outgassed SiC surface to a Si flux at a temperature of  $800^\circ\text{C}$ . A subsequent 5 min annealing at  $1000^\circ\text{C}$  in the absence of Si flux gives rise to the sharp pattern shown in panel (a), corresponding to the  $1 \times 1$  spots of SiC. Further annealing for 5 min at  $1100^\circ\text{C}$  produces the  $(\sqrt{3} \times \sqrt{3})R30$  reconstruction shown in panel (b). Finally, the complex  $(6\sqrt{3} \times 6\sqrt{3})R30$  pattern shown in panel (c) appears after 10 min annealing at  $1250^\circ\text{C}$ , demonstrating the formation of graphene. In different experiments, the annealing temperature can be various. It should be noticed that the first carbon layer grown on the Si-face of SiC, referred as buffer layer, is not graphene. Although the atomic arrangement of this layer is identical to that of graphene, however, unlike graphene, one third of the carbon atoms of this layer are covalently bonded to the underlying Si atoms of the topmost SiC layer. The  $\pi$ -band



**Fig. 2.** LEEM image of graphene on 6H-SiC(0001) with a nominal thickness of 1.2 ML formed by annealing in Ar ( $P=900$  mbar,  $T=1650^\circ\text{C}$ ). Copyright 2009 Nature.

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