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Toward the Reproducible Growth of Graphene on Wide SiC Steps: A Study of the Geometric Properties of 4H-SiC (0001) Substrates

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Abstract. Herein, we report an original adaptation of an XRD set-up in order to measure the miscut angle values in our 4H-SiC on axis substrates with a high precision of ± 0.02°. This study also reveals a correlation between the formation of wide steps on 4H-SiC(0001) and the relative orientation of the SiC crystalline planes versus the gas flow direction. These two results paves the way towards the reproducible growth of graphene over wide SiC steps.

Introduction

Step bunching is defined as the movement of atoms at high temperature leading to the formation of steps [1]. When graphene is grown by sublimation on the Silicon (Si) face of Silicon Carbide (SiC), step bunching takes place and continues until the buffer layer (BL) is fully formed [2]. The width and height of the SiC steps thus formed highly affect the properties of the graphene above [3].

During thermal annealing, around 1300°C in our experimental conditions, 4H-SiC(0001) will starts to undergo a surface reconstruction [4, 5]. At this stage, new steps with a certain shape, height and width begin to form. At higher temperature, around 1500°C, the BL appears. The BL is the first carbon layer that is formed during the SiC sublimation on the Si face. It is covalently bonded (for about 1/3 of its C atoms) to the Si atoms in the SiC underneath. At higher temperatures, the BL detaches from the SiC and is transformed into the first layer of graphene and, at the same time, another BL is formed underneath and so on. The complete formation of the BL hinders the surface atoms motion because of the higher energy needed for this process at this stage which would involve subsequent breaking the BL-Si bonds and re-bonding. This means that the tuning of the step's shape on the Si face of SiC can only be done before the full formation of the BL.

Yazdi *et al.* have demonstrated that each SiC polytype has its own surface energy which corresponds to the energy needed to remove a particular terrace. These authors argued that, in the case of 4H-SiC(0001), there are two different surface energies [2]. As a consequence, steps with different surface energies will have different erosion velocities during 4H-SiC(0001) sublimation. Steps with the lowest energy will have a higher erosion velocity as compared to the steps with the highest energy. Faster steps will catch up the slower ones and step bunching will take place. This phenomenon will lead to the formation of new steps that are wider (up to µm) and higher with a height above one nm [6]. This step bunching continues until the full formation of the BL which results in the stabilization of the surface [7]. This suggests that the step bunching in SiC can be fully controlled only by the choice of the polytype used and by the parameters of the growth process such as the temperature ramp, pressure, duration, temperature... However, this hypothesis alone cannot explain the formation of large steps in 4H-SiC(0001). Indeed, several experimental works have shown that the shape of steps resulting from step bunching is highly influenced by the initial miscut angle of the

SiC wafer [8]. Dimitrakopoulos *et al.*, have shown that in the case of 4H-SiC(0001), the width of steps is inversely proportional to the miscut angle with respect to the (0001) crystallographic plane. And this statement has been even confirmed for small miscut values lower than 0.5° [9].

Miscut Angle Measurement by XRD

The miscut is related to the geometry of the as received wafers and cannot be controlled. According to supplier information, our 4H-SiC(0001) are on axis with a miscut lower than 0.5°. However, with such an uncertainty it is very difficult: (i) to compare our graphene growth results from one substrate to another when originating from different wafers, and (ii) to unravel the effect of each growth parameter on the SiC steps shape. An evaluation of the miscut angle with a higher precision is needed.

Here, we report an unusual method to determine the miscut angle on SiC (0001) substrates which is based on a combined optical alignment and X-Ray Diffraction (XRD) rocking curve measurement. This technic is similar to the one used by Enslin *et al.* to determine the miscut angle on sapphire substrates [10]. The miscut angle of three SiC wafers have been determined using the method described below and the values obtained are very close. An example is presented in the following.

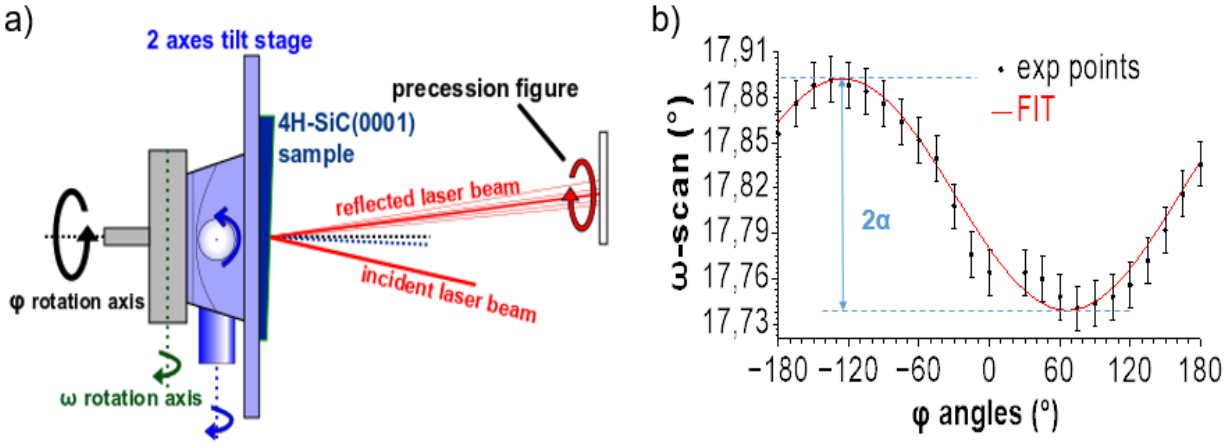

Fig. 1. (a) Scheme of the experimental setup to align the substrate's normal and the axis of the in-plane rotation (φ-axis) of the diffractometer, (b) ω–φ–XRD map of the 4H-SiC(0001), measured near the (000n) reflection, with n an integer number, indicating the miscut angle α.

First, the optical alignment is made in order to make collinear the substrate's normal and the in-plane rotation axis (φ -axis) of the diffractometer. As shown in the Fig. 1 (a), this is realized by using a 2 mm diameter laser device pointing on the center of the goniometer. The laser is reflected by the SiC surface onto a screen placed about 11 m away from the sample. This large distance allows to be highly precise on the adjustment of the sample holder tilting and to achieve an error on the angles between 0.01° and 0.02°. Aligning the surface's normal with the φ-axis consists in minimizing the amplitude of the precession figure observed on the screen. Once this alignment done, a series of rocking curves (ω-scan) on the (000n) plane (n being an integer) is made by varying φ from -180° to 180°. If the crystalline planes are tilted relative to the substrate surface (due to the miscut angle), the sample rotation around the φ-axis results in a variation of the XRD peak position in the ω-direction. In Fig. 1 (b), the ω peak position is plotted as a function of the corresponding φ angle. The resulting curve is fitted using a sinus function which amplitude, α, equals the miscut angle with respect to the SiC (0001) plane [10]. This miscut angle turned out to be lower than 0.07° ± 0.02° for our three SiC wafers. Thus, the results obtained in the same growth conditions for two samples originating from different wafers from this series can be used to address the synthesis reproducibility. Moreover, such a low miscut angle should be favorable to the growth of wide SiC steps [9].

Effect of the Crystalline Orientation vs Gas Flow Direction

After an optimization of the growth conditions, such as the temperature ramp and the environment of the growth, a homogeneous distribution of well-aligned and wide (> 6 µm) steps has been achieved as illustrated by AFM imaging (Fig. 2 (a)). However, for two out of the eight samples prepared with the same growth conditions, wide steps have not been achieved and zigzag shaped steps are observed instead. The single difference between these two samples' sets was the orientation of the substrate on its holder *after* the growth. For the wide steps samples, an unintentional rotation of 45° counter clock wise (ccw) has been observed while no rotation was observed for the ones without large steps. Besides rotation, samples unintentional translation is sometimes observed but without an effect on the width of the steps. This suggests that the orientation of the sample, *i.e.* of the 4H-SiC crystalline planes, relative to the gas flow direction during the growth has an influence on the resulting steps' shape.

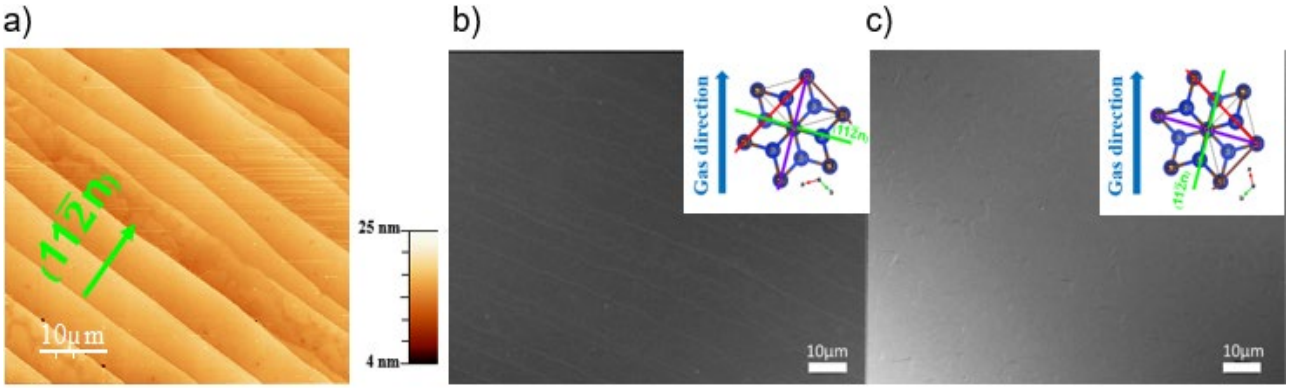

Fig. 2. (a) Topological AFM image on a sample surface that had a rotation of 45°ccw during the growth (50 µm×50 µm); (b) and (c) Optical microscopy (OM) images of a sample grown with the plan $(11\bar{2}n)$ close to perpendicular and close to parallel to the gas direction, respectively. For each OM image, the corresponding VESTA schematization is given [11].

The AFM image correlated with the crystalline directions of our 4H-SiC revealed that the steps are aligned parallel to the plane $(11\bar{2}n)$ in agreement with the work of ref [12]. The authors of [12] have demonstrated the formation of ordered steps on 4H-SiC(0001) consisting of two planes: (0001) and high-index $(11\bar{2}n)$ (n = 11;12). In order to minimize the surface energy during thermal annealing, unstable surfaces, which are tilted with respect to a stable surface, will tend to decompose into these thermodynamically stable surfaces, *i.e.* (0001) and $(11\bar{2}n)$ [13]. It is however very speculative at this stage to compare our results to these studies because they have been obtained on 4H-SiC(0001) with an off-cut with respect to the direction $[11\bar{2}0]$ or $[1\bar{1}00]$, which parameter is still unknown in our case. Moreover, none of the studies cited above took into account the effect of the gas flow direction versus the $(11\bar{2}n)$ SiC crystalline plane which could be critical as shown here.

In order to validate that our results are truly related to the direction of the gas flow, control experiments have been achieved in the very same growths experimental conditions. Before growth, samples were intentionally placed in a manner where the gas direction was close (i) to perpendicular and (ii) to parallel to the $(11\bar{2}n)$ plane. The corresponding optical microscopy images obtained after growth are shown in Fig. 2 (b) and 2 (c), respectively. In the first case, step bunching with the formation of wide and well aligned steps parallel to the plane $(11\bar{2}n)$ on the surface occurs (Fig. 2 (b)). While, in the second case, zigzag shaped steps are observed (Fig 2. (c)). This result confirms that the appearance of giant steps on the crystalline plane $(11\bar{2}n)$ depends on the relative gas flow direction.

Together with the precise characterization of the miscut angle presented in the first part, taking into account the orientation of the sample during growth allowed us to improve the control and reproducibility of our graphene samples on wide steps. As a result, a homogeneous distribution of well-aligned steps using an Ar-H_2 mix gases system has been achieved for more than 25 growths. OM and AFM characterizations (not shown) revealed that steps of 8 to 11 µm in average width are

obtained. Furthermore, Raman mapping (not shown) showed that a continuous graphene film (with up to 70% being graphene monolayer) is covering these large steps. The number of graphene layers were estimated using the ratio of the integrated intensity of the G band of graphene on the integrated intensity of the G band of a highly oriented pyrolytic graphite used as reference [14].

Summary

We have shown that an original adaptation of an XRD set-up allows to measure the very low miscut values of our SiC on axis substrates with a high precision of ± 0.02°. This parameter is essential to enable the comparison of growths carried out on different substrates. In addition, we have demonstrated the critical influence of the relative orientation of the SiC crystallographic planes versus the gas flow direction for obtaining wide and well-defined SiC steps during the SiC surface preparation stage before graphene growth. These two results pave the way towards the enhanced reproducibility of graphene growth over large SiC steps.

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