

Topography and Atomic Strain Deformation of Epitaxial Graphene on Si-terminated 6H-SiC Extended to the few Microns Order

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Abstract

Micron-extended strain characteristics of single and bilayer graphene grown on Si-terminated 6H-SiC wafers are presented. High compressively-strained graphene is obtained over the continuous graphene layer that covers the SiC processed wafer. The strength of compressive strain in single layer graphene varies gradually across terraces, while it can be uniform along terraces, especially the wider ones (~20 μm). Single layer graphene tends to show larger strain anisotropic distribution, due to abrupt variations of de/recomposed SiC topography and stronger coupling the C buffer layer. Bilayer graphene, more often found at narrower terraces (~10 μm), presents equiaxial compressive strain, as a measure of its degree of epitaxy. We propose our processing technology platform, i.e. based on the combination of SiC wafer pre-growth conditioning and specific single-step high temperature-treatment conditions, as a route to control and optimize the characteristics of graphene nanoelectronic devices on SiC.

1. Introduction

Strain engineering (SE) of materials has become an important subject of research [1]. The soundness of SE, for instance, applied to graphene is the result of the confluence of four aspects; the possibility to 1) synthesize it controllably, 2) measure strain and probe inelastic relaxation phenomena, 3) apply stresses and measure their physical-chemical properties locally and precisely, and 4) model their nanostructures and predict their properties based on ab initio calculations. The physics behind SE is a 3x3 symmetric tensor, with six independent components, i.e. all the properties of the crystal are determined by the lattice parameters and the shape of the unit cell. As graphene is a monolayer material, its strain would consist of three in-plane components, but its high bendability makes that usually out-of plane strain has to be considered too. The change of graphene properties due to deformation (elastic bending) can be understood as a flexoelectrical effect and represented by a strain gradient [1].

Two types of strain are reported, uniaxial strain and biaxial strain (isotropic). Remarkably, Raman spectroscopy appears as one of the more accurate techniques for strain parametrization mainly based on the Grüneisen parameters; as it probes graphene's phonons [2]. Specifically, Grüneisen

parameters are a measure of strain as the magnitude of a shift in phonon frequencies accounts for crystal deformations. The phonons frequency is fundamentally represented by the material's signature peaks in the Raman spectra and their position shift can be used to monitor crystal stress or deformation. Graphite-like materials can be very precisely studied by Raman scattering due to a strong cross sectional resonance [2]. For graphene, G and 2D Raman modes at ~1580 cm^{-1} and ~2690 cm^{-1} , respectively, have Grüneisen parameters $\gamma_G \approx 1.8$ and $\gamma_{2D} \approx 2.7$.

Strain of epitaxial graphene grown on SiC crystal has recently been reported. Ferralis *et al.* [3] studied the early stages of the growth by Raman spectroscopy and attributed the compressive strain of graphene deposited on Si-terminated 6H-SiC wafers to the large difference between graphene and SiC thermal expansion coefficients. Accordingly, the magnitude of the compressive strain could be controlled by processing conditions (growth time at a fixed temperature). However, no results and discussion concerning the distribution of the strain and its correlation with the substrate topography was provided. Alternatively, Robinson *et al.* [4] precisely correlated large variations in the Raman peak shifts (i.e. graphene strain non homogeneities) within very short distances, as small as 300 nm and not uniform beyond 1 μm , due to changes in the topography of the SiC by atomic force microscopy (AFM).

In this work, we synthesize and study the strain characteristics of epitaxial single and locally bilayer graphene. We correlate strain with the topography features of the SiC crystal substrate arising from the thermal treatment by both local and extended analysis of Raman spectroscopy data.

2. Experimental Materials and Results

- SiC sample processing and graphene deposition

Substrates are n-type 6H-SiC (0001) wafers ($N_D - N_A \cong 7 \times 10^{17} \text{ cm}^{-3}$) which have been sliced 3.5° off axis with respect to the basal plane and diced as 1 x 1 cm^2 samples. Chemical mechanical polishing (CMP) has been optimized to obtain atomic step terraces with well-defined edges, as described elsewhere [5]. Graphene growth is performed on the Si face of the 6H-SiC chips. The thermal treatment consists in a single step heating with temperature hold at 1550°C lasting 30 min., under vacuum. The induction heating furnace is a rapid thermal annealing system. Combined with the ex situ CMP conditioning of the SiC wafers,

a key aspect to control the thermodynamics of the SiC crystal decomposition and graphene formation is the use of a graphitic cap during high temperature treatment [6].

- Morpho-structural characterization and Discussion

Figure 1 compiles some typical results of graphene grown as specified above. OM image and 100 x 50 μm^2 mappings for a) full width half maximum (FWHM) of 2D Raman band, b) G line wavenumber and c) 2D line wavenumber are included, which correspond to two different positions in the same sample; in the sample center (left side panel) and nearby the sample edge (right side panel).

Parallel terraces of uniform and regular width, with straight edges (AFM data not shown), can be observed in both OM images. In the sample center example (left), SiC terraces are typically $\sim 20 \mu\text{m}$ in width. The area is mainly covered by single layer graphene, as understood from the predominance of FWHM $\sim 35 \text{ cm}^{-1}$ of the 2D Raman band, which can be fitted by a Lorentzian curve. In the sample edge example (right), terraces tend to be $\sim 10 \mu\text{m}$ in width. The probed area basically consists in alternate SiC terraces covered by single and bilayer layer graphene (Fig. 1 a)).

Strained-graphene features can be profoundly analyzed from the results of the G and 2D band mappings; 1) respective area distributions of the G and 2D peaks and 2) their correlation, as well as 3) local features of the peak intensities; i.e. independently for 2D and G bands. As a common and relevant feature of the whole sample, i.e. in both the sample center area and the edge scanned area, as seen in Fig.1 shifts of the peak positions align with the pattern of the discernible SiC terraces.

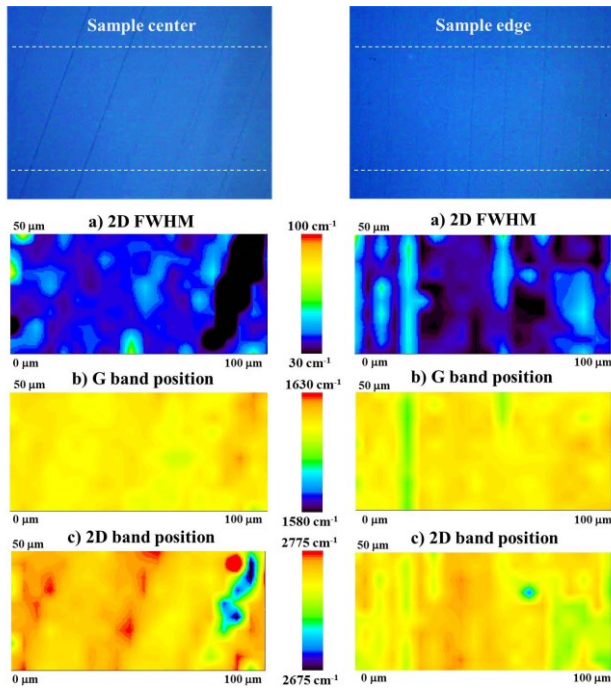


Fig. 1 x100 OM and Raman scattering of graphene grown on Si-face 3.5° off-axis cut 6H-SiC (probed area within dotted lines).

3. Discussion and Summary

Summarizing these and other data in Table 1, two important aspects are worth highlighting. There is a correspondence between the SiC terrace width and the number of layers. In present growth conditions, uniformity of grown graphene as a monolayer is related to de/re-composition of SiC forming wider terraces ($\sim 20 \mu\text{m}$). Concerning to graphene strain, grown graphene is compressive, highly strained ubiquitously. We attribute this terrace-extended characteristic as a measure of its degree of epitaxy with respect to SiC crystal support (actually tighten to the buffer layer); whereas non-uniform tension is promoted in the abrupt variations of the SiC topography; basically the steps of SiC terraces resulting from de/re-composition of the SiC substrate that leads to graphene growth.

Our investigation demonstrates that SE of epitaxial graphene on SiC is possible and can exceed the double digit micron scale. The key point is of technological nature; i.e. performing the graphene growth close to thermodynamic equilibrium [6] in combination with certain surface conditioning of the SiC wafers [5]. Our technological platform paves the way for second generation of epitaxial graphene on SiC nanoelectronic devices.

Morpho-structural features			Graphene	
SiC	Terrace	Wide >20 μm	Predominant SLG	G
			Compressive strain Biaxial strain Highly strained Non-uniform strain	Ql
			G:2D ≥ 0.5	Qt
			SLG	G
	Narrow $\sim 10 \mu\text{m}$		Compressive strain Biaxial strain Highly strained Non-uniform strain	Ql
			G:2D > 0.5	Qt
Step	Step heights 25-10 nm		SLG/BLG	G
			Compressive strain Biaxial strain Highly strained Non-uniform strain	Ql
			Very variable, including G:2D $\gg 0.5$	Qt

Table 1. Graphene strain features correlated with graphene and SiC morpho-structural characteristics. Key: G, graphene number of layers; Ql, Strain qualitative classification; Qt, quantitative strain; G:2D, G upon 2D Raman band shift ratio; SLG/BLG, single/bi-layer graphene.

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