Probing residual strain in epitaxial graphene layers on 4H-SiC(0001) with Raman spectroscopy


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Raman microspectroscopy was used to measure compressive strain within epitaxial graphene (EG) grown on the carbon-terminated SiC(0001) face as a function of annealing time for a growth temperature of 1400 °C. A maximum strain of ~0.5% was seen at the longest time of 55 min. This differs from the ~0.9% expected for strain caused by cooling from the growth temperature due to the differential thermal contraction between the SiC and EG layer, despite good agreement between this model and data on EG on SiC(0001). We suggest that this is due to the different EG bonding mechanisms on the two SiC faces.

Since being isolated experimentally in 2004,1 graphene has attracted intense research interest owing to its remarkable electronic properties,2 thus graphene systems hold great promise for advanced electronics. For graphene to become a manufacturable platform for electronics, a process for producing wafer-scale graphene sheets is required. One method proposed for this is the thermal decomposition of SiC.3 In producing wafer-scale graphene sheets is required. One method proposed for this is the thermal decomposition of SiC.3 In this process, SiC is heated to high temperatures, at least ~1200 °C but often higher, whereupon the Si preferentially evaporates away, leaving behind a C-rich surface that reconstructs to form a sp2 bonded epitaxial graphene (EG) layer.

In this work we concentrate on the growth of graphene on the C-terminated (001) face of 4H-SiC, which has been shown to provide high carrier mobilities when compared with the Si-terminated (0001) face.4 EG on the (0001) face has been shown to grow with rotational disorder between layers, rather than the Bernal stacking, causing the graphene layers to be decoupled from each other and allowing multilayer films to maintain the electronic properties associated with single-layer graphene.5

Raman microspectroscopy has been shown to be a powerful technique for characterizing graphene systems.5–12 In defect-free graphene, the characteristic Raman bands are seen at ~1580 cm−1 (G band) and ~2700 cm−1 [two-dimensional (2D) band].5 In the presence of defects, such as grain boundaries and edges, a third band is present at ~1350 cm−1 (D band). For EG grown on SiC, the Raman spectra are further complicated by the presence of the second-order SiC Raman bands that mask the graphene bands in the range of 1400–1800 cm−1, which means that a subtraction of a reference SiC spectrum is required to reveal the graphene spectrum.13

Strain can be detected as shifts in the position of the Raman bands; previous work has investigated these strains in mechanically exfoliated graphene14 and EG grown on SiC(0001).13,15 In the latter case, differences in lattice parameter and thermal expansion coefficients cause strains to build up between the graphene layers and the substrate. In this work the strain present in graphene on 4H-SiC(0001) was probed with a view to understanding the strain effects with a view to improving electronic transport in the EG films.

Sample growth was carried out on 5 × 10 mm2 chips cut from a semi-insulating 4H-SiC wafer (Cree, Inc., Durham, NC). These substrates were fitted into an aperture in a molybdenum plate and annealed under UHV (<10−10 mbar) conditions through radiative heating from a carbon heating element. A protective sapphire cap was placed between the heater and the SiC with a 1 mm separation from the surface. After cooling the samples to ambient temperature, low energy electron diffraction (LEED) measurements of the surface were performed in situ. The samples were then removed from the UHV system for further measurements. Low energy and transmission electron microscopy measurements (to be published separately) show that the graphene regions are two to three monolayers thick.

The Raman analysis was carried out with a Renishaw microspectrometer with the sample excited using a 633 nm HeNe laser. The laser power was typically 4 mW with a spot size of ~5 μm, which was focused with a ×50 lens. The spectral resolution was estimated to be ~6 cm−1 based on the full width at half maximum of a silicon 520 cm−1 peak. For measurement purposes we describe the surface of the chip in terms of regions, which we term “ranks,” along its length (see the inset of Fig. 3). The typical measurement process involved taking four 30 s scans in each rank, with eight being taken in the central “rank 1” region. Analysis here focuses on the 2D band, which is situated away from the substrate spectral features (as shown in Fig. 1), removing the need for background subtraction. As shown in the inset of Fig. 1, the 2D peaks are fitted by a Lorentzian function with any linear background having already been leveled. The fit allows a smaller experimental uncertainty in the peak centroid, typically ±0.5 cm−1, than the bare spectrometer resolution.

The position of this peak was then compared to the value obtained for freestanding exfoliated graphene of 2642 cm−1,6 and a peak shift relative to this datum was calculated. The Raman shift Δω/ω that arises from a given strain tensor εij is given by

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Previous work that concentrated on measuring strain values for EG grown on SiC(0001) for similar annealing times at a growth temperature of 1300 °C found that the results could be fitted very well by a model, whereby the compressive strain is generated by the difference in thermal expansion coefficients between the graphene and the SiC substrate as they are cooled from a state of mechanical equilibrium at the growth temperature. The largest strain was obtained for the longest (60 min) anneal times. In this model the relationship between strain and thermal expansion coefficient is given by

$$\frac{1}{1 - \varepsilon} = \exp \left( \int_{T_\text{RT}}^{T_g} \Delta \alpha(T^*)dT^* \right),$$

(2)

where $\Delta \alpha$ is the difference in thermal expansion coefficients between the SiC $\alpha_{\text{SiC}}$ (for which a measurement may be found in Ref. 17) and graphene $\alpha_g$ (for which a calculation may be found in Ref. 16). It is approximately constant within the range of temperatures covered here from RT up to the growth temperature ($T_g$=1400 °C) and has a value of $\Delta \alpha=\pm 6.5 \times 10^{-6}$ K$^{-1}$. If we apply Eq. (2) to the data we have obtained here for EG on the SiC(0001) face, then a maximum strain of $-0.9\%$ is expected, which is rather larger than the maximum $-0.5\%$ observed in Fig. 2. This is our main result here.

Work elsewhere has been carried out showing the formation of pleats within graphene layers on both SiC(0001) (Ref. 18) and SiC(0001) (Ref. 19) formed as a strain relief mechanism, which will limit the maximum strain achievable. Atomic force micrographs (not shown), however, reveal no evidence for such pleats in any of our samples, ruling out this possibility as an explanation. We also see no evidence in these images for the presence of nanocrystalline graphite, which can also give rise to Raman shifts.

On the other hand, this discrepancy could arise if an hour-long anneal does not yield a strain-free mechanical equilibrium state at the growth temperature we used. This is a possibility we cannot exclude as we have not characterized our sample at high temperature. It is also known that EG layers are not strongly bonded to the SiC(0001) substrate, which allows for some strain relaxation as the system contracts during cooling from the growth temperature.

As well as variations in 2D peak positions between samples with differing anneal times, we have also observed some variation within single 5 × 10 mm$^2$ samples. Figure 3 shows how there can be a large variation in 2D peak position within single samples with different anneal times at the 1400 °C growth temperature, with the 2D Raman peak positions plotted for each “rank.”

Samples annealed for short times are very uniform, with small Raman shifts, indicating that little graphitization has occurred at this point. Such samples show areas with a graphene-growth precursor reconstruction in the LEED patterns [see Fig. 4(b)], indicating a far-from-complete graphene film. The positive (tensile) strains seen at low annealing times (Fig. 2) may well be connected with this reconstruction. Those samples annealed for around 30 min show the most variation across the chip, with large Raman shifts at the edges (higher numbered ranks) indicating that there is a thermal gradient across the chip, with the edges first to be graphitized: they will be hotter as they are in
physical contact with the molybdenum plate, which absorbs more radiative heat. Finally, samples annealed for the longest times show a relatively uniform large Raman shift compared to the maximum observed here, indicating that graphitized material now covers the entire (001) surface of the SiC. A typical LEED pattern is shown in Fig. 4(a), with the usual broken ring structure of misaligned graphene layers superimposed on the substrate spots, indicating the presence of rotational disorder and concomitant weak interlayer bonding.

To summarize, it has been shown in this work that increasing the annealing time in UHV for graphene growth on SiC(0001) at a growth temperature of 1400 °C increases the compressive strain present within the graphene layer(s) to a maximum value of ~0.5% for a 55 min anneal. The apparent gradual increase in strain observed when spatially averaging all the data is shown to result from thermal gradients across our chip surfaces, with a fairly abrupt jump from very low strains to $\epsilon \approx -0.5\%$ once graphitization takes place. This is a process that starts at the ends of the chip and progresses toward the center, taking 40–45 min to cover the entire chip under the conditions we used here. We attribute the discrepancy in the maximum strain value observed, which is lower than previously observed on SiC(0001), to the graphene layer decoupling from the substrate when grown on SiC(0001). We attribute this shortfall in strain as being due to rotational mis-stacking of the EG layers leading to weak bonding and partial strain relief. Understanding the mechanisms that cause strain to build up within EG films is important as strains have been shown to control electronic properties such as band gaps and carrier mobilities.

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2N. M. R. Peres, Rev. Mod. Phys. 82, 2673 (2010).