Supplementary data

**Epitaxial graphene on SiC: Modification of structural and electron transport properties by substrate pretreatment**

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**Graphene Growth**

Samples from the same wafer are compared in this study. Moreover, other samples also from other SiC wafers have been tested. A total number of 23 samples showed a shallow stepped surface after graphene growth on Ar pretreated SiC substrates. All these samples are taken from wafers with a very low nominal mis-orientation of (-0.06°/-0.01°, -0.01°/-0.01°, 0.01°/0.06° towards major [11°00] / minor flat [11°20]). Although, the two samples from the latter wafer (miscut of 0.01°/0.06°) showed no homogenous morphology. The results are similar for graphene growth at 1900 °C, 1850 °C, 1800 °C.

H₂ pretreatment of the SiC surface results in giant step bunching after graphenization which was confirmed by corresponding growth runs with samples from the four mentioned wafers.

The formation of shallowly stepped surfaces by Ar pre-annealing seems to be a very sensitive process which depends on the chemical cleaning of the SiC substrates as well as on the state of the reactor. We used chemical-mechanical polished (CMP) wafer with an epi-ready coating from II/VI Deutschland GmbH. Prior to cutting the SiC wafer (Automatic dicing saw DISCO DAD 3220 and diamond resin bond blades) the surface was protected by a thin layer of photoresist. An ultra-sonic cleaning in propanol and aceton of the individual samples seems to be sufficient in order to obtain the described type of shallowly stepped graphene layers. It has turned out that a further wet-chemical cleaning of the substrates by RCA clean (standard clean 2 or standard clean 1+2) or by oxygen-plasma treatment is counterproductive. This leads to giant step bunching during the graphenization process.

Moreover, the condition of the reactor plays also an important role in order to obtain graphene on shallow stepped terraces. No shallowly stepped surfaces were obtained when H₂ gas was used in the reactor prior to Ar pretreatment and graphene growth. At least one dummy graphenization run is necessary to get rid of residual effects. Other particle related deteriorations of the shallow stepped surface were observed.

**Micro-Raman measurements**
Raman spectroscopic measurements were acquired to examine the structural quality of the graphene sample using a *LabRAM Aramis* Raman spectrometer (*Horiba*) operated in backscattering mode. The spatial Raman imaging across an area of (30 x 30) µm² was performed with a frequency-doubled Nd:YAG-Laser with a wavelength of 532 nm, a 100x objective (NA 0.95) and a piezo sample stage with a step size of 0.2 µm, whereat the laser power was kept very low to avoid local heating of the graphene sample. A total number of 14,520 Raman spectra were recorded from this area. The laser spot diameter is about 1 µm. The effective lateral resolution is estimated to about 0.8 µm due to oversampling and the intensity profile of the spot.

![Figure 1](image_url)

**Figure 1.** Raman spectra of (a) pure SiC substrate, (b) an epitaxial graphene layer and (c) an exfoliated graphene sheet.

Figure 1(b) shows a single Raman measurement of a shallowly stepped graphene sample. The graphene related G line close to 1600 cm⁻¹ and the 2D line around 2750 cm⁻¹ is clearly visible. [1] A broad SiC overtone as can be seen in the spectrum of pure SiC (figure 1(a)) overlaps the G peak in the range between 1500 cm⁻¹ and 1900 cm⁻¹ which unfortunately complicates the evaluation of its peak properties by Lorentzian curve fitting. [1] Additionally, no defect peak (D peak) around 1350 cm⁻¹ appears (1(b), 1(c)).
Since the 2D peak is not affected by the broad SiC overtone signal these peaks are evaluated by Lorentzian curve fitting. The full width at half maximum (FWHM) of the 2D peak is extracted and plotted in the 2D-FWHM topography maps because this value is related to the number of graphene layers.[1] Figure 2 gives an overview of the Raman 2D-FWHM topography map (30 µm x 30 µm) of an epitaxial graphene layer grown at 1900 °C in Ar atmosphere on four different positions (A-D), which are denoted by red dots. In positions A and B the FWHM value of 31 cm⁻¹ is attributed to single layer graphene, whereas the positions C and D with FWHM of 65 cm⁻¹ and 61 cm⁻¹ are attributed to bilayer graphene according to [1].

**Figure 2.** Typical examples of Lorentzian curve fitting of the 2D peaks for an epitaxial graphene layer grown on an Ar pre-annealed substrate. The red dots in 2D-FWHM maps denote the measurement position.

The total FWHM distribution of epitaxial graphene grown at 1900 °C in Ar atmosphere as a function of the 2D peak position is shown in figure 3. The scatter plot and the FWHM bar chart clearly shows that the majority of 2D linewidths are scattered around 34 cm⁻¹ with a standard deviation of 4 cm⁻¹, which emphasizes that this sample is mainly covered with monolayer graphene. A very small number of 2D peaks shows FWHM values larger than 40 cm⁻¹. An exact assignment of the values to bilayer graphene is difficult because of the lateral resolution of the measurement. For a conservative estimate of the area covered with bilayer graphene we attribute FWHM values larger as 45 cm⁻¹ to bilayer graphene.
Figure 3. Histogram of the FWHM values and its distribution as a function of the 2D peak position for the 14520 data points from the 30 µm x 30 µm topographic map of the shallowly stepped graphene layer.

By counting the scattered data points between 30 to 45 cm\(^{-1}\) and 45 to 60 cm\(^{-1}\) we estimate the approximate amount of monolayer and bilayer graphene, respectively, covering the measured sample area of (30 x 30) µm\(^2\). Approximately 97 % of the sample area is covered by monolayer graphene and approximately 3 % of the area is covered with bilayer graphene. Figure 3 also reveals a wide spread of the 2D peak position from 2725 cm\(^{-1}\) to 2755 cm\(^{-1}\) with a mean 2D peak position of 2736 cm\(^{-1}\) and a standard deviation of 2 cm\(^{-1}\), which is associated with an average G peak position of 1604 cm\(^{-1}\) and a standard deviation of 2 cm\(^{-1}\). Both peaks are shifted to higher wavenumbers and significantly differ from the peak positions of exfoliated graphene (figure 1(b) and 1(c)). As mentioned before by [2], this effect is related to strain induced into the graphene lattice by interacting with the SiC substrate. Due to the different thermal expansion coefficients of SiC and graphene, a significant blue shift of both G and 2D peak arises in the Raman spectrum. On the other hand the blue shift of the G peak is also strongly connected to the doping level in the graphene layer [3], although the 2D peak position is rather weakly affected. The G linewidth is another important feature to assess whether strain or doping is present in the graphene layer. Unfortunately, because of SiC overtone that overlaps the G peak, the evaluation of the G peak linewidth is complicated. Subtracting the Raman spectrum of epitaxial graphene by a reference spectrum of pure SiC often produces additional noise and artifacts, which affects the line shape of the G peak. Therefore, both effects strain and doping cannot be excluded.
SEM Measurements

For scanning electron microscopy (SEM) we used an in-lens detector at 3.2 mm working distance and an acceleration voltage of 1 keV. With these settings we obtained high resolution images of our graphene samples. SEM images of SiC substrates after annealing in argon atmosphere at 1400°C show also areas of different contrast as can be seen in figure 4(a) in the paper. The absence of graphene related Raman signals prove that no graphene has formed. The areas of different contrast are therefore attributed to buffer layer domains (detected by characteristic LEED pattern) and uncovered SiC surface areas. The dark areas are attributed to buffer layer domains because other samples show that longer annealing times (compared to 30 min for the sample in figure 4) result in an enlargement of the dark areas. In general, the assignment is difficult. The contrast can change within minutes of SEM inspection and depends on the scan speed which is probably due to sample charging effects. Note that for the main statement in the paper (namely that buffer layer stripes have formed after annealing in Ar atmosphere) the assignment is irrelevant because the dark and the bright stripes in figure 4(a) are very similar.

AFM measurements

In AFM measurements it is difficult to observe the buffer layer stripes because of their very shallow height. A height of about 0.3 ±0.1 nm is observed for the stripes located at the upper edge of the terrace steps. The material sensitive AFM phase images clearly show stripes of different contrast. In figure 3(c) the buffer layer stripes are not well resolved. The small islands can be resolved because they are taller, about 0.5 ±0.1 nm. They are attributed to buffer layer domains on remaining SiC islands.

References

