

Supporting Information

Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition

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1. Fabrication methods

Our fabrication procedure starts with the evaporation of a 500 nm Ni film on a SiO₂/Si substrate. Next, the Ni coated substrates (1-2 cm² in size) are loaded into a CVD chamber and heated at 900 °C-1000 °C under the flow of 600 sccm and 500 sccm of Ar and H₂, respectively, for 10-20 minutes. Ni grains with atomically flat surfaces and sizes of 1-20 μm form during this

annealing step. The CVD growth is carried out at 900 °C or 1000°C with a 5-25 sccm and 1500 sccm flow of CH₄ and H₂, respectively, for 5 to 10 minutes. Once the CVD synthesis is finished, the graphene film is released by protecting the graphene film with Poly[methyl methacrylate] (PMMA) and etching the underlying Ni with a mild HCl aqueous solution (~3% vol.). Subsequently, the film can be transferred to any substrate for analysis and characterization. Once the PMMA/graphene film is on the target substrate, the PMMA is dissolved and removed by acetone. In the case of graphene transfer from a patterned Ni geometry, a PMMA layer was also spin-coated on the Ni/graphene surface. Afterwards, HCl was also used to etch the patterned Ni. The sample is then treated with a NaOH solution to detach the PMMA layer sections which are in contact with the SiO₂ surface. NaOH partially etches the surface of SiO₂, starting at the side edges of the sample, leading to the complete detachment of the graphene/PMMA membrane (see ref. 17).

2. Electron diffraction of the CVD graphene films

Electron diffraction patterns on the graphene films change from one location to another. The major difference observed is the appearance of secondary sets of diffraction spots also with hexagonal symmetry but with a mis-orientation with respect to the most prominent diffraction spots (see arrows in Fig. S1). This occurs due to either the inexact normal incidence of the electron beam on a multilayer region or some degree of mis-orientation between layers. Two representative diffraction patterns are shown in Figure S1 a and Figure S1 b displaying the observations described above. It is important to note that no ring-like diffraction patterns are observed. Ring-like patterns are expected for

either a thick graphite film with random stacking of the graphene layers or a thin film of amorphous carbon.

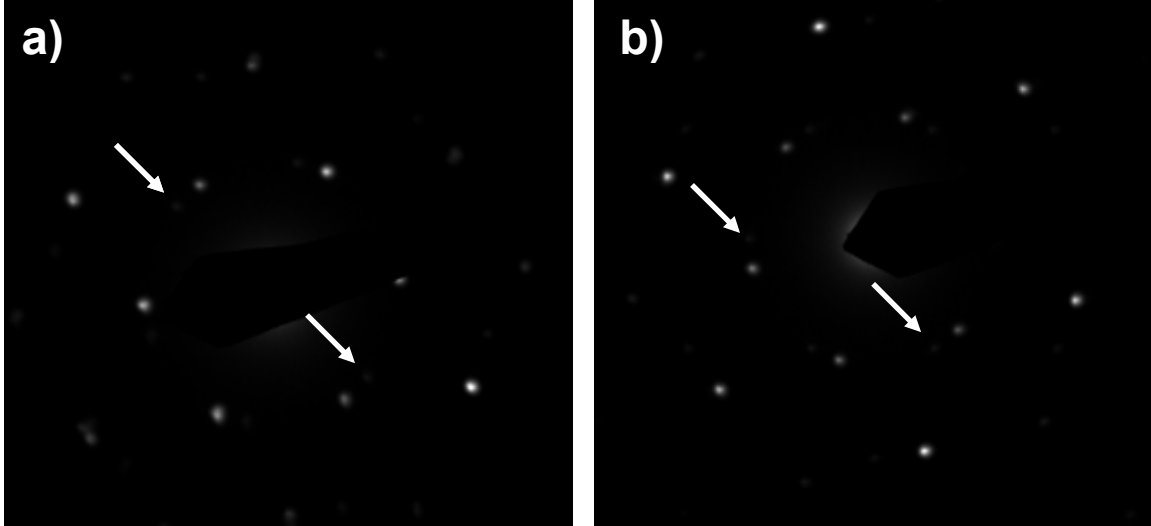


Figure S1. a, Electron diffraction of a multilayer region on a graphene film. **b,** Electron diffraction image of a different multilayer region. Arrows indicate secondary diffraction spots observed due to either a misorientation between adjacent graphene layers or a deviation from perpendicular incidence of the electron beam on the graphene film.

3. Raman spectroscopy of 1-2 graphene layers on Ni grains

Regions of single- and bi-layer graphene grow mostly on the largest grains of the Ni film. This explains why we observe large regions ($\sim 20\ \mu\text{m}$) with single and bi-layer graphene after transferring the film to SiO_2/Si . Optical microscopy (Fig. S2 a) of the Ni film after CVD shows opaque or brown color regions on top of the smallest grains (indicated by red arrows). These are identified as multilayer graphene by Raman spectroscopy (Fig. S2 b). It can be seen from Fig. S2 a, that it is very hard to identify the graphene grown on the

surface of the largest grains (indicated by black arrows). This is because only one to two graphene layers grow on their surface as suggested by the Raman spectra taken on the surface of these grains (Fig. S2 b).

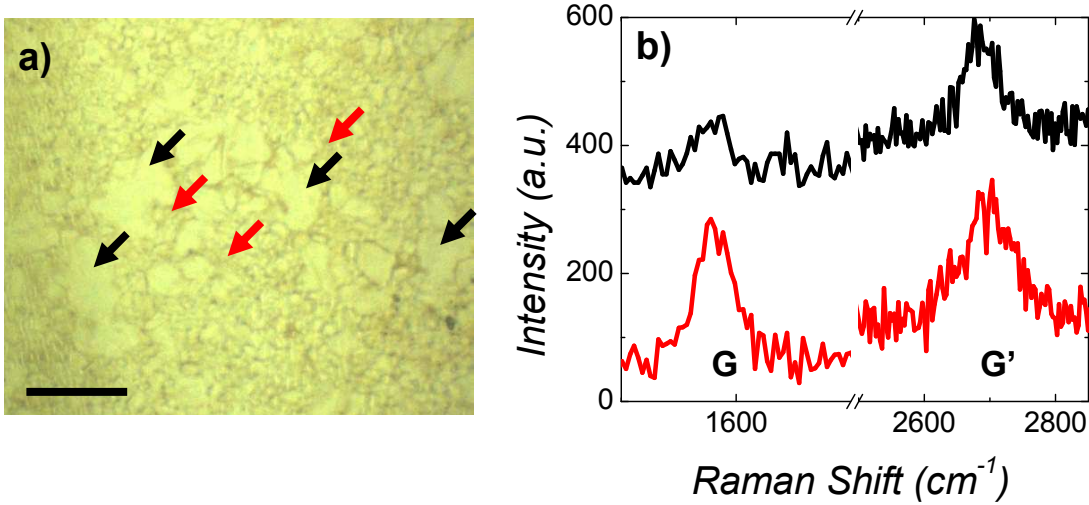


Figure S2. **a**, Optical image of a Ni film after growing a graphene film by CVD. **b**, Representative Raman spectra of the regions identified by the arrows in the optical image in (a). Regions consisting of multiple layers of graphene (3 or more) can be distinguished in the optical image as brown features (indicated by red arrows). These are usually on top of the smallest grains of the microstructure of the Ni film. They have $I_G/I_{G'}$ ratios of 1.5-3 and G' linewidths of $\sim 70 \text{ cm}^{-1}$, indicating multilayer graphene regions (see Figure S3 and S5). Grains of 20-40 μm size (indicated by black arrows) do not show opaque tones in the optical images. Raman spectra taken at several locations on the surface of these grains (black arrows) always show low $I_G/I_{G'}$ (0.5-1) ratios and relatively narrow G' linewidths (30-40 cm^{-1}). These are characteristic features of the Raman spectra of 1 to 2 graphene layers. The scale bar in **a** is 50 μm

4. Multilayer graphene preferential nucleation at grain boundaries:

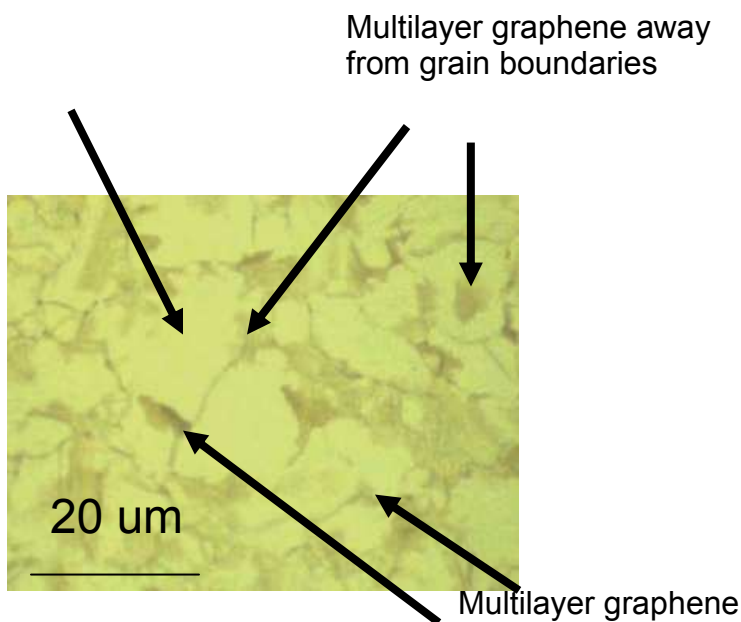
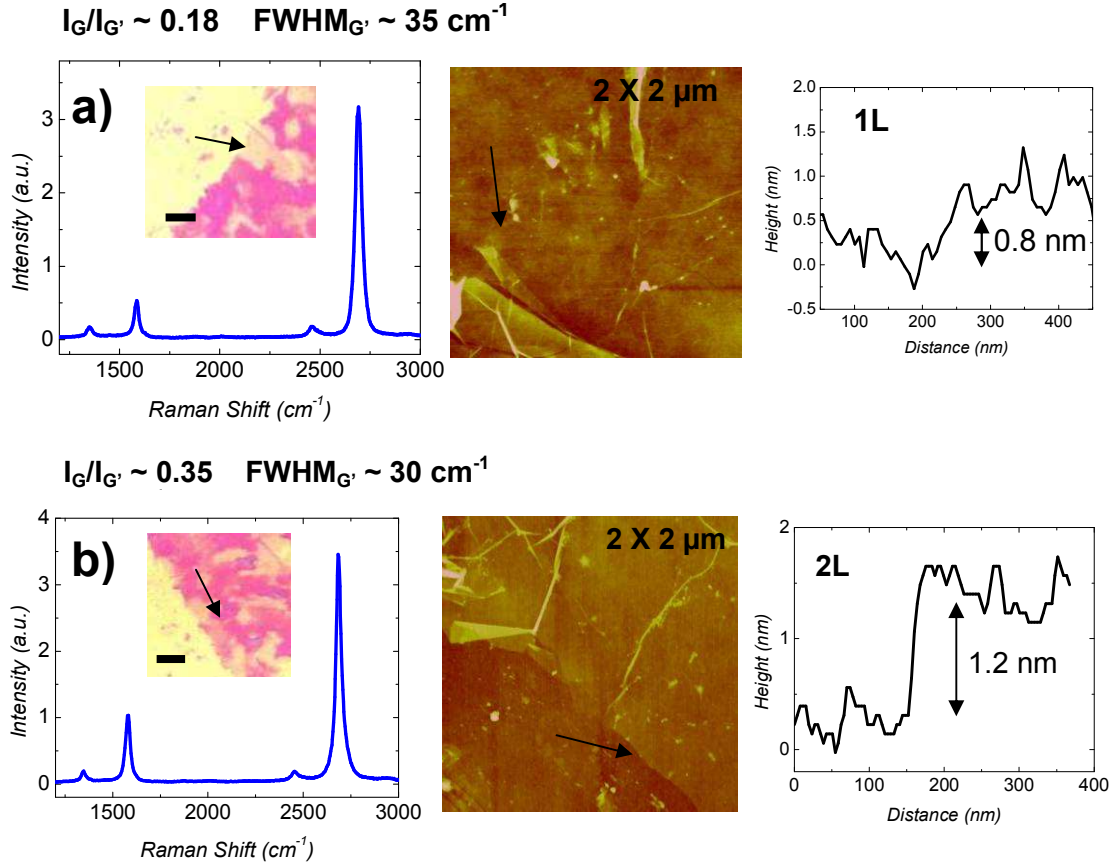


Figure S3. Optical image of multilayer graphene (dark brown regions pointed by arrows) which preferentially nucleates around grain boundaries. Occasionally (but less frequently) multilayer graphene also nucleates away from the grain boundaries

5. Correlation of the $I_G/I_{G'}$ peak intensity ratio with the height of film regions as measured by AFM

AFM, optical microscopy and Raman spectroscopy of specific regions on a graphene film were undertaken to confirm the relationship between the G to G' intensity ratio ($I_G/I_{G'}$) and the number of graphene layers. For this, Raman spectra were taken at the regions shown by the AFM images and optical images of Figures S4 a, b and c which correspond to 1, 2 and ~3 layers of CVD grown graphene, respectively. AFM scans correspond to the area pointed out by the arrow in the optical image. Height profiles are also shown (measured at the location indicated by the arrow in the AFM images). Note the

correlation between the color contrast in the optical images and the number of layers measured by AFM. Measuring the $I_G/I_{G'}$ ratio provides a method for the fast estimation of number of the layers under the optical microscope, similarly to the case of mechanically cleaved graphene.



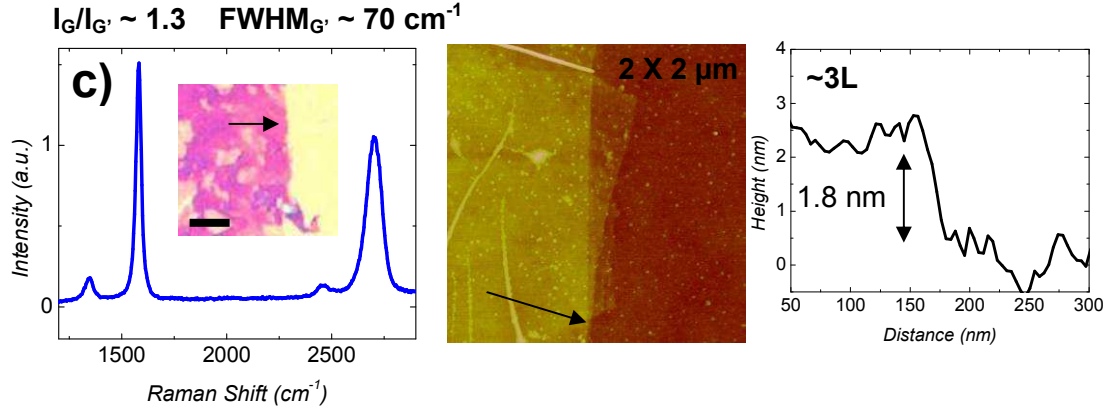


Figure S4. a-c, Raman spectra, optical and AFM images of regions consisting of 1 (a), 2 (b) and ~ 3 (c) graphene layers. Scale bars for optical images in the insets for the Raman spectra are $3 \mu\text{m}$.

6. Graphene film roughness

Figure S4 is a $100 \mu\text{m}^2$ area AFM image of the graphene film shown in Fig. 1d. From this image we can obtain film roughness information. The mean and RMS roughness are measured to be 1.97 nm and 3.27 nm, respectively. The roughness measurements correspond to the height data of the entire AFM scan shown in Fig. S5. The mean and RMS roughness estimations were obtained in the following way:

$$R_m = \frac{1}{n} \sum_{j=1}^n |Z_j|$$

$$R_{rms} = \sqrt{\frac{\sum_{j=1}^n (Z_j)^2}{n}}$$

where R_m is the mean roughness and R_{rms} is the RMS roughness, and Z_j is the surface height deviation as measured from the mean height of the data in Fig. S5.

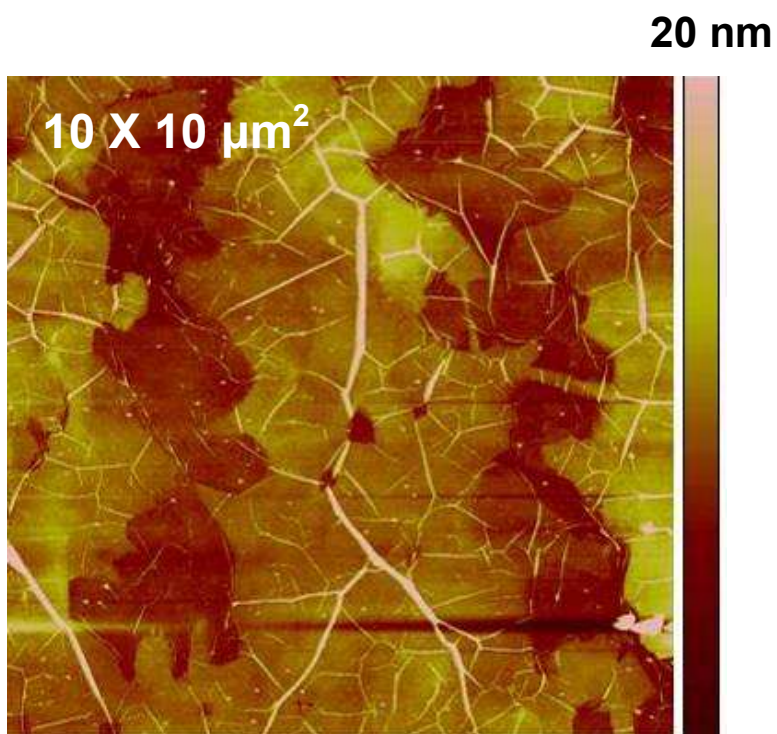


Figure S5. AFM image of a CVD graphene film after being transferred to a SiO₂/Si substrate. The color scale (right) indicates increased height of the graphene film.