Electron Diffraction data of CVD grown graphene

The electron diffraction pattern was recorded with a JEOL-3000F operated at 100kV. It shows the typical six-fold symmetry expected for graphene and graphite. Electron diffraction spots were labelled using Miller-Bravais (hkil) indices. The analysis of the diffraction intensity ratio $I_{(0-110)} / I_{(1-210)}$ (on the right) was carried out in order to identify whether the investigated flake was a mono- or a multi-layer graphene. The ratio $I_{(0-110)} / I_{(1-210)}$ of 1.38 reveals that the flake is in fact a single-layer[1,2]
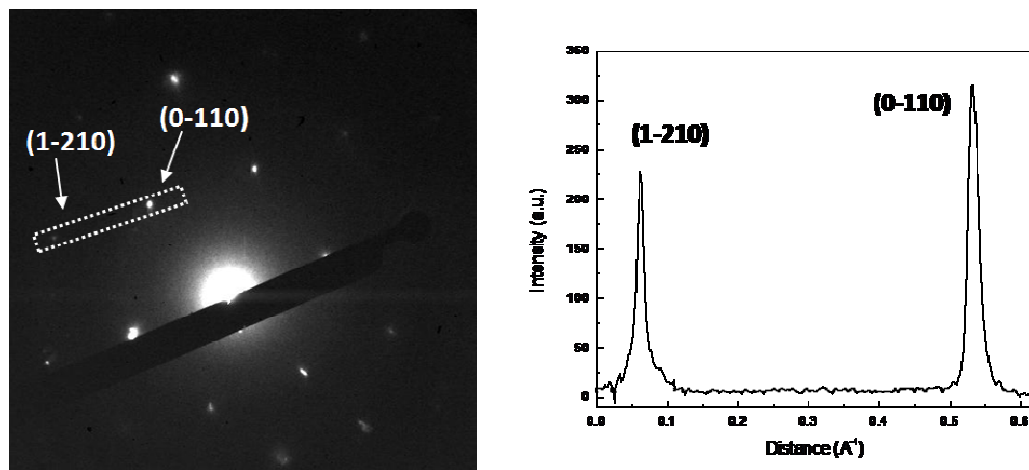

Fig S1 a) ED differection pattern of a CVD grown graphene film. b) Diffraction intensity $I_{(0-110)} / I_{(1-210)}$ of the (0-110) and 1-220) peaks.

1. Horiuchi, S. *et al.* Carbon Nanofilm with a New Structure and Property. *Jpn. J. Appl. Phys.*, 2003, **42**, L1073.

2. Meyer, J.C. *et al.* On the roughness of single- and bi-layer graphene membranes. *Solid State Comm.*, 2007, **143**, 101.

EDX data of CVD grown graphene films transferred to silicon samples

The analysis shows that there is a hardly noticeable amount of Ni present in our films after transfer, The Ni peak lies below the detection limit of approximately 1%.
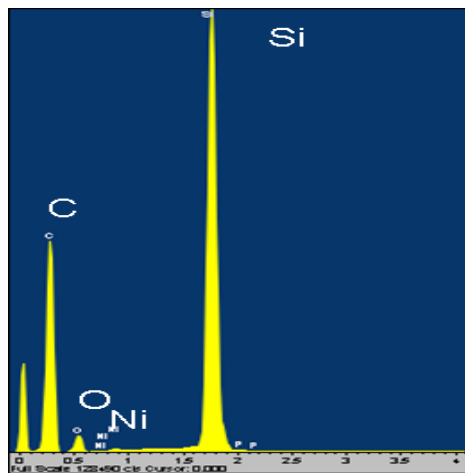

Fig S2 EDX spectrum of a graphene film transferred onto SiO_2

Calculations for solubility and diffusivity of carbon in Ni at different temperatures.

The solubility and diffusivity of carbon in Ni as a function of temperature (T) can be described by the empirical formulae[1]:

$\ln S = 2.480 - 4880/T$, where S is the solubility in grams of carbon per 100 grams of nickel and,

$\ln D = 0.909 - 20200/T$, where D is in cm^2/s.

Using these formulae for $T_1 = 1023K$ and $T_2 = 1223K$ gives, $S(T_1) = 0.46\ S(T_2)$ and $D(T_1) = 0.04\ D(T_2)$.

The square root of product of diffusivity and time has dimension of length and is proportional to diffusion length (l_D), which is a scaling constant determining the extent of diffusion (for example a simple solution of Fick's law is $n(x,t) = n(0,t)\ \mathrm{erfc}(x/2l_D)$). Lowering the diffusivity by a factor of 0.04 is equivalent to decreasing the diffusion time by 0.04 times but keeping the diffusivity constant.

1. Lander, J.J., Kern, H.E. & Beach, A.L. Solubility and Diffusion Coefficient of Carbon in Nickel: Reaction Rates of Nickel-Carbon Alloys with Barium Oxide, *J. Appl. Phys* 1952, **23**, 1305.

Raman Characterisation of graphene

Raman spectroscopy is a powerful tool for characterisation of various carbon materials including graphene[1-2]. The principal peaks observed in graphene are the *D*, *G* and *2D* peaks at ~1330 cm^{-1}, ~1580 cm^{-1} and ~2660 cm^{-1} respectively, using a excitation wavelength of 632.8 nm. The *G* peak stems from in plane vibrations and has E_{2g} symmetry; this is observed in all sp^2 carbon systems. The *D* peak is related to defects and disorder and stems from breathing modes of A_{1g} symmetry in sp^2 systems[1]. This transition is forbidden in perfect graphitic systems and requires a defect for its activation, and so is observed at the edges of graphene samples[3, 4, 5] or on doped graphene samples[6]. Highly disordered carbon materials such as pyrolytic carbon exhibit strong and broad *D* peaks indicating their nanocrystalline nature. The ratio of *D* to *G* peaks is seen to scale with decreasing crystallite size.

The *2D* peak is a second order of the *D* peak but is seen even in non disordered systems, due to the fourth order phonon momentum exchange double resonance process. This is an intervalley process and does not require a defect for activation and plays a crucial role in the characterisation of graphene[7, 8]. The *2D* peak is a single peak in monolayer graphene, a combination of 4 peaks in bilayer graphene, and approaches a standard graphite *2D* band after 5-10 layers[7]. The intensity I(*2D*)/I(*G*) is approximately 4 for monolayer graphene[7] and decreases with the addition of subsequent layers, thus making it possible to estimate the thickness of graphene layers.

To investigate graphene growth in the initial stages we took Raman spectra after short growth times. Figure S1 shows Raman spectra for graphene films grown with dwell times from 30 sec to 300 sec, at 950 °C, at 1 Torr. The spectra clearly show that thickness of films increases from mono- to multi-layered graphene to thicker graphtic layer (>10 layers) with increasing growth time.
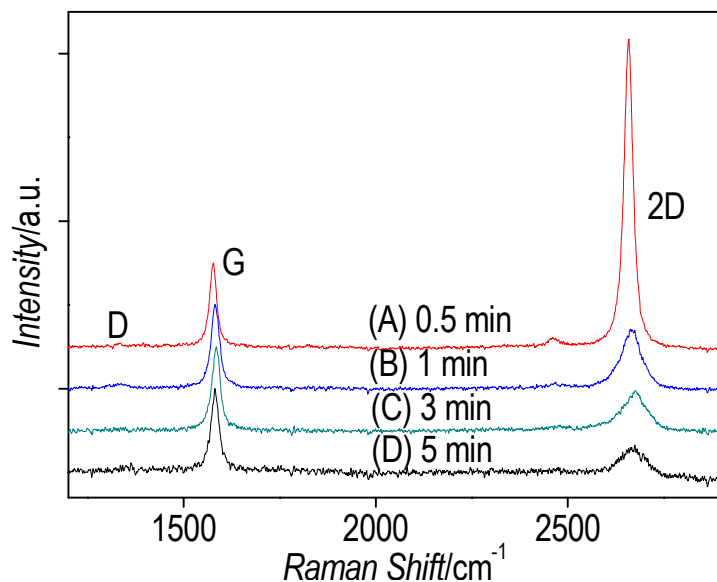
Fig. S3. Initial stages of CVD graphene growth. Raman spectra (A), (B), (C) and (D) of graphene films on Ni after growth times of 0.5, 1, 3 and 5 minutes respectively. The decreasing *2D/G* ratios from (A) to (D) (3.7, 0.74, 0.48 and 0.33 respectively) indicate increase in thickness of graphene[1], from monolayer (A) to >10 layers (D).

1. Ferrari, A.C. & Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B, 2000,* **61**, 14095.
2. Dresselhaus, M.S., Dresselhaus, G., Saito, R. & Jorio, A. Raman spectroscopy of carbon nanotubes. *Physics Reports*, 2005, **409**, 47.
3. Casiraghi, C. et al. Raman Spectroscopy of Graphene Edges. *Nano Letters*, 2009, **9**, 1433.
4. Graf, D. et al. Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene. *Nano Letters*, 2007, **7**, 238.
5. Gupta, A.K., Russin, T.J., Gutiurrez, H.R. & Eklund, P.C. Probing Graphene Edges via Raman Scattering. *ACS Nano*, 2009, **3**, 45.
6. Wei, D. et al. Synthesis of N-Doped Graphene by Chemical Vapor Deposition and Its Electrical Properties. *Nano Letters*, 2009, **9**, 1752.
7. Ferrari, A.C. et al. Raman Spectrum of Graphene and Graphene Layers. *Physical Review Letters*, 2006, **97**, 187401.
8. Malard, L.M., Pimenta, M.A., Dresselhaus, G. & Dresselhaus, M.S. Raman spectroscopy in graphene. *Physics Reports*, 2009, **473**, 51.