Rapid Thermal CVD of Graphene on Copper

Sanna Arpiainen[1], Olli Svensk[2], Wonjae Kim[2], Markku Kainlauri[1], Hua Jiang[3], and Harri Lipsanen[2]

[1]VTT Microsystems and Nanoelectronics, Micronova, P.O.Box 1000, FI-02044 VTT, Espoo, Finland
[2]Aalto University, Dept. of Micro- and Nanosciences, P.O.Box 3500, FI-00076 AALTO, Espoo, Finland
[3] Aalto University, Dept. of Applied Physics, P.O.Box 15100, FI-00076 AALTO, Espoo, Finland
sanna.arpiainen@vtt.fi

We have studied the chemical vapor deposition (CVD) of graphene in a cold wall reactor designed for rapid thermal processing (RTP) of semiconductors. In addition to the fast operation, the advantages of this reactor type are complete control over the process parameters like temperature gradient which would allow increasing the reactor size up to several meters and compatibility to batch type processing on smaller substrates. The deposition parameters like temperature, methane flow and CH_4/H_2 ratio were optimized at different pressures between 7 and 80 Torr. The composition of the deposited film was characterized with scanning confocal µ-Raman spectroscopy and verified with TEM.

The optimization was performed simultaneously with the process chamber modification. The basis of the process is direct infrared (IR) heating that is provided through a quartz window located at the top of the 8" chamber. Radiation is absorbed by SiC covered graphite susceptor and the heat is transferred into the copper foil attached to it. The temperature is controlled on the basis of the optical pyrometer reading from the susceptor back surface. By increasing the measurement points and control electronics, the IR power could be adjusted *in situ* to provide homogeneous thermal gradient over the chamber, though currently the power profile is calibrated separately. The minimum pressure in the deposition chamber is currently limited to 7 Torr, which is somewhat higher than the optimal 0.5 Torr reported [1].

As expected, the optimal deposition parameters and graphene quality were found to be strongly dependent of the pressure. At high pressures significant amount of hydrogen was required to provide counterbalance to methane pyrolysis that would produce soot or amorphous carbon over all surfaces. Though the deposition parameters could be adjusted to produce graphite, monolayer graphene growth was rare. Under otherwise optimized conditions, the monolayer graphene began to dominate at 16 Torr and the crystalline quality improved with further reduction of the pressure as determined from the decrease of the height of the Raman D peak (1350 cm^{-1}) that has been associated with defect states [2]. When reducing the pressure, the optimal CH_4/H_2 ratio increased from 0.3 to 4, while the deposition temperature was kept close to 1000 ºC. Highest quality graphene was achieved at the lowest achievable pressure, thus further improvement is expected with increased pump capacity.

The Raman spectra (fig. 1) measured from the samples after transfer to a HfO_2 layer indicate continuous graphene, composed of monolayer graphene with about 5 - 10 % coverage of thicker graphene. This is clearly illustrated in SEM images (fig. 2) taken before and after the transfer. The thicker regions are located on large surface corrugations in the copper foil. Electrical analysis of the graphene indicates otherwise good quality; after vacuum cleaning the Dirac point is at zero and the sheet resistivity is close to exfoliated graphene. Mobility measurements are under progress.

The crystalline quality of graphene was further analyzed with HR-TEM (fig. 3). The graphene was transferred with pmma to copper grid with holey carbon support and cleaned with acetone, though all pmma could not be properly removed due to simultaneous etching of the support. TEM imaging revealed continuous graphene lattice extending well beyond the shown 30 nm area, with electron diffraction pattern confirming the monolayer thickness and perfect hexagonal lattice. These results confirm the ability to produce large graphene crystallites at pressures above the UHV conditions.

References

[1] X. Li, C.W. Magnuson, A. Venugopal, J. An, J.W. Suk, B. Han, M. Borysiak, W. Cai, A. Velamakanni, Y. Zhu, L. Fu, E.M. Vogel, E. Voelkl, L. Colombo, and R.S. Ruoff, Nano Letters **10** (2010) 4328.
[2] A.C. Ferrari, Solid State Communications **143** (2007) 47.

Figures

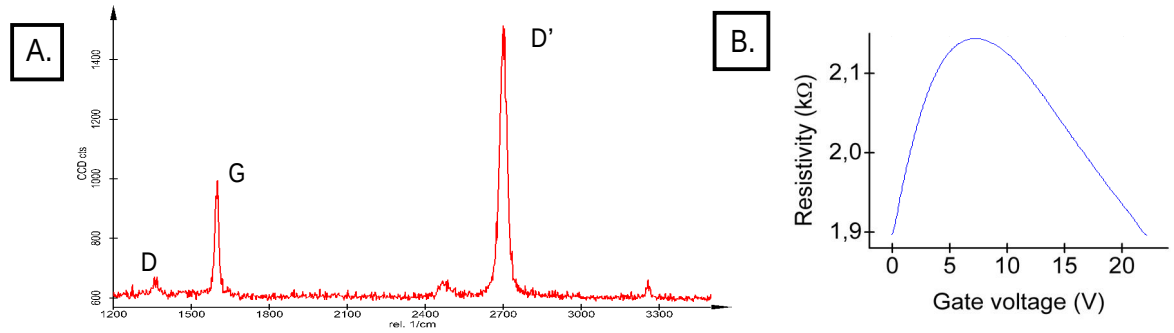

Figure 1 Raman spectrum (a) and resistivity (b) of transferred CVD graphene on 40 nm thick HfO_2. The Raman spectrum is averaged over a 20 x 20 μm^2 area, excluding the darker multilayer spots shown in figure 2. Measurement was done using WITec alpha 300 R with 532 nm excitation laser. The sheet resistivity as a function of gate voltage shows behavior typical to graphene. Here the Dirac point is still shifted after copper etch induced doping.

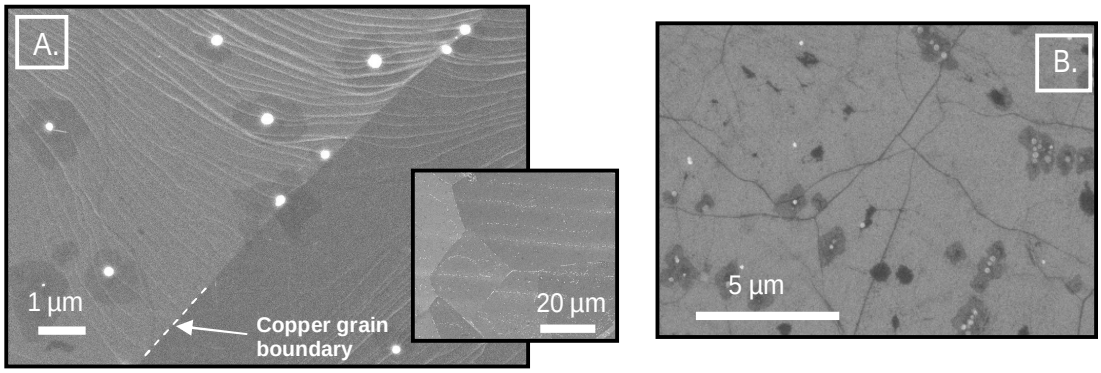

Figure 2 SEM images of continuous graphene deposited on a copper foil. (a) As deposited graphene on copper, showing the atomic terraces and grain boundaries in copper. The spots with thicker graphene (darker areas) are concentrated into the grooves in the foil (inset). (b) Transferred graphene on hafnium oxide, also illustrating the wrinkles caused by the difference in thermal expansion coefficients of copper and graphene.

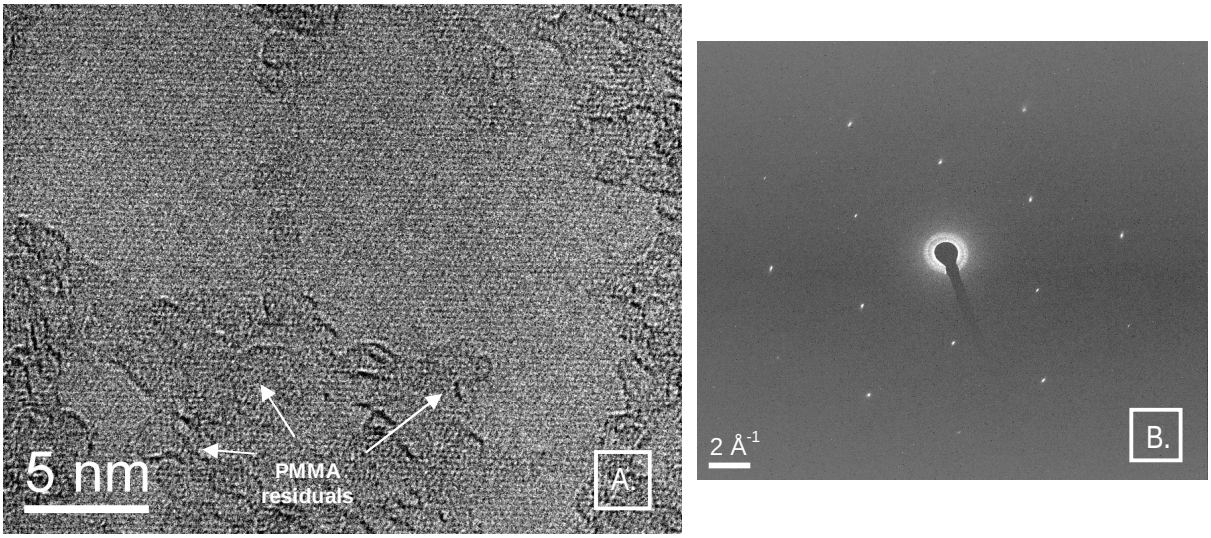

Figure 3 TEM image (a) and diffraction pattern (b) of suspended graphene grown from methane at 7 Torr in a cold wall CVD reactor. The image shows a continuous lattice, though partly under pmma residuals from the transfer process. Diffraction pattern through the whole image area indicates perfect monolayer graphene with single lattice orientation. Similar pattern was measured throughout the sample, also on areas totally under pmma, with no indication of orientational variants related to small misoriented grains. The images were measured using Cs-corrected TEM (JEOL 2200FS) at 80 kV.