Graphene Functionalized and Optically Forged by Femtosecond Laser

Andreas Johansson[1,2], Pasi Myllyperkiö[1], Pekka Koskinen[2], Jukka Aumanen[1], Juha Koivistoinen[1], Hung-Chieh Tsai[3], Chia-Hao Chen[4], Lo-Yueh Chang[4], Vesa-Matti Hiltunen[2], Jyrki J. Manninen[2], Kamila Mentel[1], Wei Yen Woon[3], Mika Pettersson[1]

[1,2]Nanoscience Center, Department of Chemistry[1], and Physics[2], P.O. Box 35, FI-40014, University of Jyväskylä, Finland
[3]Department of Physics, National Central University, Jungli, 32054, Taiwan, Republic of China
[4]National Synchrotron Radiation Research Center, Hsinchu, 30076, Taiwan, Republic of China
Corresponding author: andreas.johansson@jyu.fi

Laser irradiation can be used for modifying properties of graphene. As an example, we have found graphene can be functionalized with oxygen-containing groups through femtosecond pulse irradiation in air [1]. We have characterized the resulting graphene oxide, using µm-XPS, and found that the chemical composition can be controlled, with varying fractions of hydroxyl and epoxy groups strongly dominating [2]. The two-photon functionalization method therefore allows tailoring of local functionalization with a patterning line width of about 300 nm. It may be used for tuning electronic properties of graphene, e.g. resistivity over five orders of magnitude [1], or its chemical reactivity which may be used for creating complex graphene-based structures. An example of graphene patterning is shown in Fig. 1a and 1b.

When irradiation is performed in inert atmosphere such as nitrogen, an unexpected phenomenon occurs: graphene detaches from the substrate and forms stable, elevated plateaus at the irradiated areas. By controlling local irradiation dose, the height of the plateaus can be varied from about 1 nm to more than 100 nm enabling drawing of complex 3D shapes from graphene simply with a laser beam. This is demonstrated in Fig. 1c, which shows an AFM image of a pyramid made by laser irradiation of graphene. This method is termed optical forging in which a pulsed laser beam forges a graphene sheet into controlled 3D shapes in the nanoscale [3]. The forging mechanism is based on laser-induced local expansion of graphene, as suggested by computer simulations using thin sheet elasticity theory (see Fig. 1d). The expansion is presumably caused by laser irradiation induced formation of defects into the graphene lattice.

The optical functionalization and forging concepts presented here offers new methods for fabricating complex graphene structures, which may provide solutions for building integrated circuitry from layered materials.

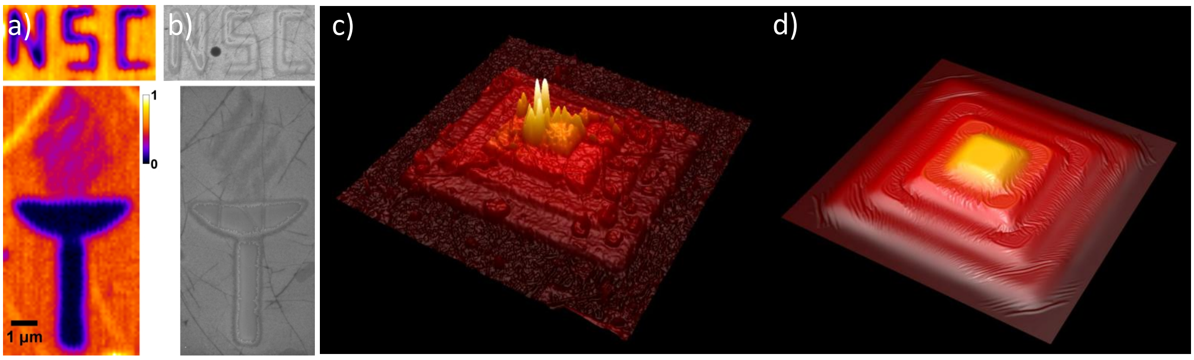

Figure 1. Monolayer CVD graphene on silicon chip. From left, two-photon oxidation patterning imaged with (a) four-wave mixing and (b) scanning electron microscopy. (c) AFM image of a pyramid shape fabricated by optical forging. The side is 11 µm and the maximum height is ~60 nm. (d) Simulation (elasticity modelling) of the same pyramid.

[1] J. Aumanen, A. Johansson, J. Koivistoinen, P. Myllyperkiö and M. Pettersson. Nanoscale, **7**, 2851 (2015).
[2] A. Johansson, H.-C. Tsai, J. Aumanen, J. Koivistoinen, P. Myllyperkiö, Y.-Z. Hung, M.-C. Chuang, C.-C- Chen, W.-Y. Woon and M. Pettersson, Carbon, **115**, 77 (2017).
[3] A. Johansson, P. Myllyperkiö, P. Koskinen, J. Aumanen, J. Koivistoinen, H.-C. Tsai, C.-H. Chen, L.- Y. Chang, V.-M. Hiltunen, J. J. Manninen, W. Y. Woon and M. Pettersson, Nano Letters, **17**, 6469 (2017).