Final report 2013

project 66p20

Characterization of graphene based catalytic systems by low energy ion scattering

Stanislav Průša, doc. Ing. Ph.D., assistant professor
Institute of Physical Engineering
Faculty of Mechanical Engineering
Brno University of Technology (BUT)
Technická 2, 616 69 Brno, Czech Republic
prusa@fme.vutbr.cz

Peter Bauer, a.Univ.-Prof. Dr., Professor
Institut fuer Experimentalphysik
Johannes Kepler Universitaet Linz
Altenbergerstrasse 69, A-4040 Linz, Austria
peter.bauer@jku.at

Introduction

The project proposal was focussed to preparation of graphene surfaces and deposition of metallic nanoparticles onto them. Originally proposed two years project was shortened to one year. All proposed first year activities were fulfilled and additional to that some of the second year activities were done as well.

Time table of activities curried out in 2013 year

1. Graphene growth at copper foil (April).
2. Graphene transfer to silicon substrate (April, May).
3. Graphene characterisation by LEIS, XPS, SIMS and TDS (May – December).
4. Graphene sample characterisation by AES, LEIS and RBS (July).
5. Deposition of gold nanoparticles at graphene samples and imaging by SEM (November).
6. One week visit of S. Prusa and R, Duda at JKU Linz (July).
7. Two days visit of P. Bauer, D. Roth and D. Gobl in BUT (November).

1. Graphene preparation

The graphene layer was grown by a standard Chemical vapour deposition (CVD) procedure [1] from methane at a cooper foil of high purity. The synthesis took place in the hot own at temperature 1000 C which is close to melting point of cupper (S. Průša).

2. Graphene transfer to silicon substrate

The graphene was transferred onto a silicon substrate in the following steps: after spin coating by PMMA the copper foil was reduced by wet etching (Fe(NO3)3 9H2O), the graphene-PMMA foil was pulled out of the solution and for several times immersed into a fresh water bath. The graphene-PMMA foil was put on a silicon substrate from the final bath and air dried, finally the PMMA layer was reduced by acetone and IPA. After that the sample surface was rinsed in H2O and blown by nitrogen (S. Průša).

3. Graphene characterisation (BUT)

First characterisation took place in Brno University of Technology (BUT), after the sample was prepared. All used analytical techniques (XPS, LEIS and TDS) have detected the presence of heavy metal contamination. The trace of tin has been detected by XPS, but as the surface sensitivity of this method is limited to a few nanometres, the location of contamination could not be identified. Thanks to extreme surface sensitivity of LEIS technique we were able to confirm the presence of this contamination close to graphene layer (R. Duda, P. Babor, T. Šikola, S. Průša).

4. Graphene characterisation (JKU Linz)

The selected samples were analysed at Johanes Kepler University Linz by high resolution LEIS, Auger Electron Spectroscopy (AES) and Rutherford Back Scattering (RBS). These techniques have confirmed the tin contamination and additional to this have proved presence of iron contamination. TRBS simulation of the ion scattering spectra (Figure 1) indicates presence of almost continues layer of metallic contamination between the graphene and silicon oxide layers. This is a serious factor which

can strongly influence the behaviour of graphene layer in electronic systems (D. Roth, P. Bauer, R. Duda, S. Průša).

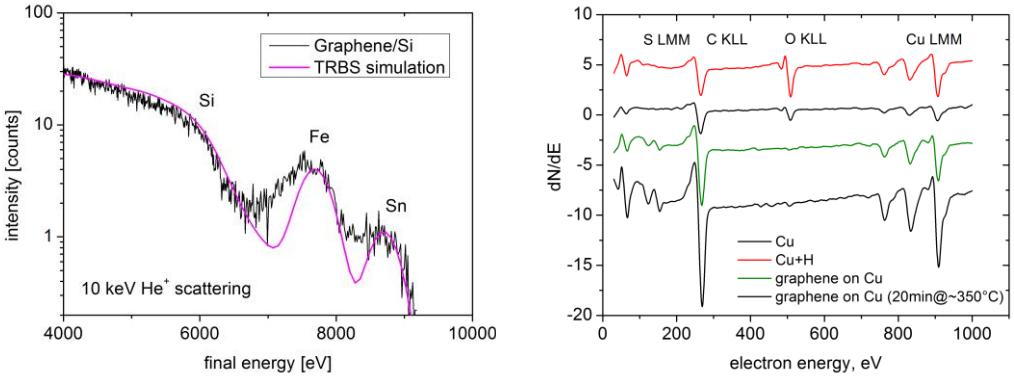
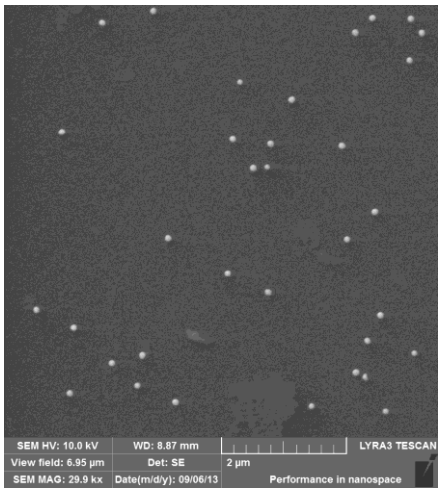


Figure 1: *LEIS spectrum of graphene silicon sample indicates tin and iron contamination visible in front of broad silicon peak (background). AES of thermally heated graphene/silicon samples confirmed homogeneous graphene film.*

5. Deposition of gold nanoparticles at graphene samples and imaging by SEM



The gold nanoparticles of various diameters (30-100 nm) were deposited at selected samples (silicon substrates and silicon with graphene layer) from colloidal solution. They were studied by LEIS and imagined by Scanning electron microscopy (SEM) at BUT. The LEIS analysis has clearly identified the gold peak at the spectrum, while SEM has imagined particle distribution at the sample surface (Figure 2) (P. Babor, R. Duda, S. Průša).

Figure 2: *SEM image of gold nanoparticles (100 nm in diameter) deposited at graphene. The presence of residual PMMA contamination is visible at the bottom.*

Scientific visits

The essential part of the project were the scientific visits of both groups in BUT and JKUL. The graphene samples have been prepared at BUT. They were analysed in situ and ex situ at BUT and JKUL. There were two scientific visits between the collaborating groups within the last year.

1. Six-day visit of project proposer S. Průša and a Czech PhD student R. Duda at JKU Linz – participation on the ion scattering (LEIS, RBS), AES experiments and data simulation, July 2013.
2. Two-day visit of the Austrian applicant P. Bauer and an Austrian PhD students D. Göbl and D. Roth at BUT - discussions on experimental results measured at JKU Linz and BUT, participation in a seminar, excursion to the labs, a lecture of P. Bauer within an regular BUT surface science group meeting „Electronic energy loss processes for slow H and He ions in metals and insulators: new insights" November 2013.

Financial costs description

540 EUR – six-day stay (6 x 90 EUR) of S. Průša at JKU Linz (14-19. 7. 2013)
540 EUR – six-day stay (6 x 90 EUR) of R. Duda at JKU Linz (14-19. 7. 2013)
348 EUR – travel expenses Linz/Brno for P. Bauer, D. Göbl and D. Roth

4 319 CZK – travel cost Brno/Linz for S. Průša and R. Duda
300 CZK – toll sticker for Austrian highways
50 CZK – road tax CZ
2 078 CZK – accommodation costs for hotel stay of P. Bauer, D. Göbl and D. Roth
2 200 CZK – subsistence for two day stay of P. Bauer, D. Göbl and D. Roth (26.-27.11.2013)

Total expenses **1428 EUR** and **8947 CZK.**

Comment to financial costs

The 4669 CZK (4319+300+50) have covered expenses of travel to Linz and back to Brno by a car for S. Průša and R. Duda. This cost was charged according to travel rules of Brno University of Technology and it is lower than the price of two return train tickets Brno/Linz (5428 CZK). The travel by car was helpful also with respect to transport of samples to be analyzed in JKUL and related necessary equipment.

The unspent money have been returned to Aktion (14 052,32 CZK to deposit account of Ministry of Education Youth and Sport of Czech Republic).

Summary

The graphene layers has been prepared by CVD method and wet transferred to silicon substrates. Residual contamination of graphene by PMMA was reduced by annealing at 400 C under ultrahigh vacuum conditions. Gold nanoparticles were deposited from colloidal solution at the top of them. Complex in situ and ex situ analysis by LEIS, XPS, TDS, AES and RBS have confirmed presence of continuous graphene layer free of pinholes. Contamination by iron and tin is concentrated between the graphene layer and silicon oxide. The iron contamination comes most probably from etching solution while tin contamination origins from the supporting copper foil. The tin is natural element which is used in copper preparation. A negligible tin contamination of high purity copper foil is selectively concentrated during the wet etching at the bottom of graphene layer.

These are important results of one year Aktion project. LEIS has showed its potential to perform reliable analysis of such surface specific system. The experiments and scientific discussions between the collaborating groups at BUT and JKU Linz have fulfilled the proposed program and have opened several courses for further investigations and possible publication.

References

[1] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, Large-area synthesis of high quality and uniform graphene films on copper foils. Science, Vol.324, 1312-1314 (2009).

Brno 30. 1. 2014

Stanislav Průša