13C labelled graphen and TLG obtained by ion implantation at high temperature on monocristalline and polycrystalline nickel

F. Le Normand*, F. Aweke*, C. Speisser*, J. Arabski**, G. Guttierez*, F. Antoni*, D. Muller*, G. Morvan***

*** :** ICube/ MaCEPV (Materials for Electronic Components and PhotoVoltaics), University of Strasbourg and CNRS, Building n° 28, Office n° 6, 23, rue du Loess, BP 20 CR 67037 STRASBOURG Cedex 2, FRANCE

** : IPCMS University of Strasbourg and CNRS, Building 69, 23 rue du Loess BP 43 67034 STRASBOURG, Cedex 2, FRANCE

***: Laboratory of Hydrology and GEochemistry (LHyGeS), University of Strasbourg and CNRS, 1, rue Blessig , 67084 STRASBOURG Cedex, FRANCE

Contact@E-mail: francois.le-normand@unistra.fr

Abstract

The graphene is a 2D hexagonal network of sp^2-hybridized carbon atoms whose successful preparation has been reported recently. In a very short time many outstanding electronic transport properties have been measured on the graphene prepared by exfoliation from Highly Oriented Pyrolytic Graphite (HOPG). Reaching these properties reveals however strongly depending on the way to prepare and to handle it. Moreover the exfoliation method is not scalable and not reproducible. Therefore many alternative elaboration methods have been described in the literature, based on chemical synthesis, on the high temperature Si layer evaporation from a SiC monocrystalline surface, on the lower temperature surface segregation of carbon absorbed into metals, like Ni or Ru, by Chemical Vapor Deposition (CVD), on the carbon adsorption on copper by CVD, or on the bulk diffusion of carbon across metallic matrices from solid sources. In this method of elaboration presented here the carbon was introduced into a carbon-diffusive metallic matrix like Ni by ion implantation. After the implantation step, thermal treatments were achieved to diffuse carbon towards either the surface or the interface between the film and the substrate. This way of preparation of graphene or thin-layers-graphite (TLG) displays potentially many advantages over the CVD process: i) Accurate and uniform control of the carbon dose; ii) Accurate depth localization of the carbon inside the metallic matrix through managing the ion energy, therefore the growth of graphene is likely to occur at the interface metal/substrate rather than at the surface according to the energy of carbon ion, to the carbon solubility and to the carbon diffusion into the matrix; iii) No necessity for gaseous decomposition of the carbon-precursor molecule like in CVD; iv) Direct integration into electronic devices of the interface graphene after dissolution of the metallic film is possible; v) possibility to use labelled 13C carbon and therefore to give insight into mechanistic studies. In the literature, the implantations were performed at room temperature followed by a thermal post-treatment [1-5]. We present here for the first time high temperature (450-600°C) implantation of carbon, thus mixing the subsequent steps of carbon implantation and thermal post treatment into one single step (Scheme 1). It is therefore expected to activate the carbon diffusion and to minimize the implantation defects. The influence of the temperature (450-600°C) and the carbon dose (from 0.2 to 4 equivalent graphen layer (EGM) will be presented. The samples studied were Ni films of 200nm thick deposited on SiO_2(300nm)/Si(100) and on monocristalline Ni(111)(200-300 nm)/MgO(111) prepared by Molecular beam Epitaxy. Most of the carbon implanted directly diffuses to the surface, forming thin layers graphite (TLG). A progressive structuration of these graphitic fragments occurs with increasing the implantation temperature. The overall carbon concentration inside and at the surface of the nickel films was determined for the first time by nuclear reaction analysis (NRA) (Figure 1), surprisingly exceeding the expected carbon concentration. This discrepancy shows that some carbon is incorporated during the different steps of the process and is involved into the TLG formation [6]. Therefore the carbon implantations were systematically studied with labeled 13C and the determination of the 13C and 12C content were determined by NRA analyses (Figure 1) and imaged by Raman spectroscopy (Figure 2). 12C was introduced at different step of the process and these carbon impurities was nuclei center for aggregation of rich-13C graphene fragments. The role of Rapid Thermal treatments is also underlined to obtain momolayer graphene films.

References

[1] Baraton L. et al, International Patent 0805769, 2008.
[2] Garaj S, Hubbard W, Golovchenko JA. Appl. Phys Lett 2010; 97, 183103
[3] Baraton L, He Z, Lee CS, Maurice JL, Cojocaru CS, Gourgues-Lorenzon AF, et al. Nanotechnology 2011; 22, 085601
[4] Mun JH, Lim SK, Cho BJ. J Electrochem Soc 2012; 159, G89-G92.
[5] Zhang R, Zhang ZD, Wang ZS, Wang SX, Wang W, Fu DJ, et al. Appl Phys Lett 2012, 101, 011905.
[6] G. Gutierrez, D. Muller, F. Antoni, C. Speisser, F. Aweke, Y. Le Gall, C.S Lee, C.S Cojocaru, F. Le Normand, submitted
[7] G. Gutierrez, F. Aweke, D. Muller, C. Speisser, F. Le Normand, submitted.

Figures

Scheme 1: Scheme of the process: a) RBS spectrum, b) SRIM simulation of the carbon distribution profile after implantation at 20 keV in Ni(200nm)/SiO_2(300nm)/Si

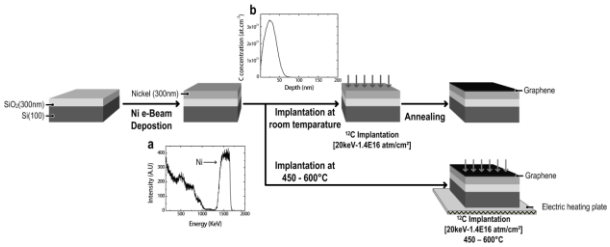

Figure 1: Nuclear Reaction Analysis inside and on the surface of Ni(111)/MgO(111) of the (a) $^{12}C(d, p)^{13}C$ reaction and (b) $^{13}C(d, p)^{14}C$ reaction.

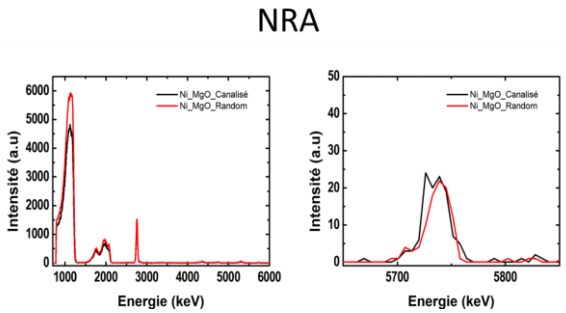

Figure 3: (a) Raman spectra on the samples implanted at 600°C with ^{13}C and ^{12}C (blue: ^{12}C, red: ^{13}C), (b) optical images and (c) corresponding Raman mapping on the position of the 2D band for the ^{13}C implanted sample at 600°C.