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Multi-layer graphene obtained by high temperature carbon implantation into nickel films

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ABSTRACT

We present a study of carbon implantation in a stacked layered substrate made of Ni(200 nm)/SiO_2(300 nm)/Si(100). The carbon atoms have energy of 20 keV. Simultaneous or subsequent heat treatment is performed in the 450–600 °C range. The carbon dose was set to be 4 equivalent graphene monolayers (EGM). Most of the carbon implanted diffuses directly to the surface, forming multi-layer graphene (MLG). A progressive structuration of these graphitic fragments occurs with the increase of the implantation temperature. However, this structuration is more pronounced if the thermal treatment is performed in situ following the carbon implantation at room temperature. The mean MLG thickness, corresponding to around 4–5 EGM, was measured by angular X-ray Photoemission Spectroscopy. Moreover, the overall carbon concentration inside and at the limits of the nickel films, determined by nuclear reaction analysis (NRA), is in the 7–10 EGM range. This concentration depends on the temperature but it exceeds surprisingly the expected carbon concentration. This discrepancy shows that some carbon is incorporated along the different steps. NRA analyses of the preparation confirm this point. To obtain large film, the presented results stress the interest to better understand the full system carbon–nickel in the preparation of MLG at each step of the process.

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1. Introduction

The graphene is a 2D hexagonal network of sp^2-hybridized carbon atoms whose successful preparation has been reported recently [1]. In a very short time, many outstanding electronic transport properties have been reported on the graphene prepared by exfoliation from Highly Oriented Pyrolytic Graphite (HOPG) [2–4]. To achieve these properties is however strongly dependent on the preparation and the handling of this material [5]. Moreover the exfoliation method is not scalable and not reproducible. Therefore many alternative elaboration processes have been described in the literature, based on chemical synthesis [6], on the high temperature Si layer evaporation from a SiC monocrystalline surface [7–9], on the lower temperature surface segregation of carbon absorbed into metals, like Ni or Ru, by Chemical Vapor Deposition (CVD) [10–17], on the carbon adsorption on copper by CVD [18–19], or on the bulk diffusion of carbon across metallic matrices from solid sources [20–23]. All these methods have currently their advantages and their drawbacks, which are depending on the expected application. In this work, we will systematically study a process derived from the CVD carbon

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surface segregation on a metallic matrix. In this method of elaboration, recently patented [24] and published [25–28], 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 even to the interface between the film and the substrate. This new way of preparation of graphene or multi-layer graphene (MLG) 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 could 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. Thus this process may be fully compatible with current microelectronic processes and the silicon technology. Literature investigations have shown that the formation of multi-layer graphene (MLG) was indeed obtained [25–28]. However the implantations were performed at room temperature followed by a thermal post-treatment. We present here for the first time high temperature (450–600 °C) implantation of carbon, thus mixing into one single step carbon implantation and thermal post treatment. By this high temperature process, it is therefore expected to activate the carbon diffusion and to minimize the implantation defects. Another report has been devoted to the influence of carbon dose and thermal post-treatments within 450–900 °C [29] after implantation at room temperature.

2. Experimental

Si(100) substrates were oxidized at 1100 °C in order to grow a 300 nm thermal-SiO_2 layer. To remove the organic residues off the substrates, the substrates were dipped into trichloroethylene while heating at 100 °C during 30 min, rinsed successively into acetone, isopropyl alcohol, cleaned in a Piranha solution 30 min at 150 °C, rinsed with deionized water and finally dried under nitrogen. After this cleaning step, 200 nm thick Ni films were evaporated by electron beam deposition at room temperature with a deposition rate lower than 0.3 nm s^{-1} at a base pressure of 2.7×10^{-7} mbar. ^{12}C ions at an energy of 20 keV and a fluence of 1.4×10^{16} at.cm^{-2} corresponding to around 4 equivalent graphene monolayers (EGM; one EGM corresponds to 3.6×10^{15} at.cm^{-2}) were implanted on these Ni (200 nm)/SiO_2 (300 nm)/Si samples. These implantations were achieved on the 200 kV EATON implanter of ICube provided with a heated substrate holder in Inconel alloy. The temperature of the surface sample was calibrated with one thermocouple permanently settled on the back near the surface of the substrate holder and a filament extinction pyrometer monitoring directly the sample surface temperature.

In order to decorrelate the synergetic effect of implantation and temperature, two kinds of sample were prepared. The first set of samples was implanted at a pressure vacuum of 2×10^{-6} mbar at 450 °C, 525 °C and 600 °C, respectively. They were further named I-T where T is the implantation temperature. The samples were maintained at each temperature for 1 h which corresponds to the implantation duration. Other samples named I-RT and I-RT-600 were implanted at room temperature and subsequently annealed at 600 °C inside the implantation chamber in similar conditions (4 EGM, 2×10^{-6} mbar, 1 h), respectively. In both cases, the heating and cooling rates were estimated to be around 60 °C min^{-1}. The implantation conditions were determined using the SRIM 2010 software which simulates the carbon profile at room temperature for an amorphous material [30]. The carbon distribution profile results in a quasi-Gaussian curve centered around 27 nm depth. The sputtering due to implantation has been determined to 2.9 nm by using SRIM. This result is in good agreement with the Rutherford Backscattering spectra (RBS) obtained before and after implantation which highlight no significant thickness evolution of the Ni film (Supplementary Materials S1).

A scheme of the overall process is given in Fig. 1.

Ion beam analyses were performed using the 4MV Van De Graff accelerator facility of ICube. RBS was used to determine the thicknesses of the Ni and SiO_2 layers before and after the implantation and/or thermal post-treatments. RBS experiments were carried out with a 2 MeV incident alpha particles beam (1×1 mm^2) and a 160° scattering angle. Moreover, to determine the evolution of C and O concentrations after each treatment, Nuclear Reaction Analyses (NRA) were performed. The $^{12}C(d, p)^{13}C$, $^{16}O(d, p_1)^{17}O$ and $^{16}O(d, p_0)^{17}O$ reactions were investigated with a 900 keV deuterons beam (1×1 mm^2). A 150 mm^2 silicon surface barrier detectors was mounted at an angle of 150° to the beam direction resulting in a total solid angle of $\Omega \sim 60$ msr. An absorber of 11.8 μm Mylar foil was attached above the detector to stop the alpha particles generated by the $^{16}O(d, \alpha)^{14}N$ reaction and the backscattered deuterons particles. The experimental spectra were calibrated by using bare SiO_2 and SiC samples for oxygen and carbon nuclear reactions, respectively, and the spectra were then simulated with the SAM software [31]. The error bar was estimated to around 2 EGM. Due to the low depth resolution of this analysis technique, we are not able to differentiate between the carbon surface and the carbon diluted into the Ni layer.

To characterize the surface of the implanted samples, SEM observations were carried out using a Scanning Electron Microscope (Philips XL-30S) in the Secondary Electron Image mode at low voltages (1 and 3 kV) more sensitive to the chemical contrast.

The Atomic Force Microscopy (AFM) measurements were performed on a NT-MDT Stand Alone "SMENA" set-up used in the resonant mode AFM Semicontact. Non-Contact "Golden" Silicon Cantilever NSG11 scanning probes were used with a minimum scanning step of 0.012 nm.

Raman spectroscopy was carried out using a Horiba spectrometer LabRam at 532 nm equipped with a CCD camera. Spectra were recorded using a 100× magnification, with a power energy of 0.93 mW and a fluence of 2.25 mW μm^{-2}. Above this fluence, damages of the graphene film might be observed [32].

X-ray photoemission spectra were recorded with a 150 mm hemispherical detector VSW with an overall resolution of 0.65 eV under a base pressure of 5×10^{-9} mbar using a

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