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Graphene production by dissociation of camphor molecules on nickel substrate

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ABSTRACT

A chemical vapor deposition (CVD) process for the production of continuous-high quality-graphene layers based on camphor decomposition on polycrystalline Ni foil, is demonstrated. In situ X-ray diffraction at the pyrolysis temperature of the Ni foil indicates the presence of dominant Ni <111> grains which play an important role in the carbon nucleation and growth. The topography of the grown graphene layers is studied by scanning electron microscopy and atomic force microscopy which show that the Ni surface is covered by continuous and wrinkled graphene carpets. Raman spectroscopy reveals the high quality of the graphene film which appears to be only a few monolayers thick. X-ray photoelectron spectroscopy indicates the existence of graphitic layers and the absence of any spectral features associated with carbides (Ni_xC). The proposed CVD process is a sufficient method for large scale production of graphene films.

1. Introduction

Graphene consists of carbon atoms in sp^2 bonding hybridization, arranged in a honeycomb lattice. Its extraordinary properties can have a number of applications in various fields such as nano- and bio-electronics, liquid crystal devices and ultracapacitors [1]. Geim and Novoselov [2] isolated graphene flakes of high structural quality but of small dimensions. The produced graphene flakes were isolated by the mechanical exfoliation of bulk highly oriented pyrolitic graphite, using the scotch tape technique. Motivated by the superior properties of graphene [3] and the low yield of the exfoliation methods, different processes are currently under development that aim to increase the production yield but also to deliver flakes of larger dimensions. Chemical wet etching of graphite with various treatments based on Hummers and Offeman methods [4] is an alternative approach to obtain graphene but with the presence of both oxidized carbon and structural defects on the graphene hexagonal lattice. More advanced plasma-enhanced chemical etching of graphite, leads also to the formation of higher quality graphene but still residual oxygen functional groups remain on graphene's surface [5]. A quite different approach for graphene production is the epitaxial growth on either Si or C terminated SiC single crystal surfaces after thermal decomposition of SiC due to evaporation of Si atoms [6]. This method results in wafer-scale graphene fabrication and for this reason is quite appealing for the microelectronics industry. However, the cost of single SiC crystal wafers and the very high temperature required for silicon evaporation are still important impediments for the industrial exploitation of this method.

A promising approach for the epitaxial growth of graphene is the chemical vapor deposition (CVD) of organic gasses onto appropriate catalytically active substrates. Carbon nanotubes and nanofibers have already been produced via appropriate CVD processes [7]. By introducing transition metal foils [8] in order to lower the energy barriers for thermal decomposition of carbon clusters and graphene growth, the quality of the graphene layers may approach the requirements of the semiconductor industry. While CVD grown graphene with dimensions of about cm^2 has been achieved on the above metal surfaces, wafer scale graphene areas exhibiting thicknesses ranging from one to few graphene layers have been mostly realized on Cu and Ni surfaces. For example, Ruoff et al. [9] demonstrated a copper catalyzed CVD process, in which by annealing gas mixture of methane and hydrogen at 1000 °C, large scale graphene islands with thickness of up to 3 monolayers are produced on copper substrates. Using a similar CVD process but with a polycrystalline Ni foil as a catalyst, ultrathin (up to 10 monolayers) continuous graphene films have been obtained by Reina et al. [10].

Transition metal assisted CVD graphene production by source gasses such as versatile ratios of CH_4/H_2 [11] or/and Ar [12] and C_2H_2/H_2 [13] has been reported over the last few years. These processes were carried out under high vacuum [12] or under ambient conditions [10] and from relatively high cooling rates [13] up to room temperature. However, with regards to carbon source for CVD fabrication there have been limited reports in the literature. Somani et al. [14] reported graphene

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synthesis from pyrolysis (850 °C) of camphor in Ar atmosphere on Ni surface, resulting to disorder graphitic structure with thickness of about 35 graphene monolayers. An alternative camphor based CVD synthesis which produced multi layer graphene domains of about ~1 μm wide and with an average thickness up to 13 layers was reported recently [15]. The same group had also proposed a modification of the above CVD method on Cu foil [16] but at higher temperature (1020 °C) for the production of few-layer-graphene (up to 3–4 layers). Moreover, thin films of spin-coated poly (methyl metha-crylate) (PMMA) [17], on metal surface have also been used as a solid carbon source by CVD. In this case, the growth of graphene layers is obtained by a reductive gas flow of H_2/Ar.

Comparing the two volatile solid carbon precursors such as the PMMA and camphor mentioned above, the latter has the advantage of being a natural hydrocarbon whereas PMMA is an acrylic polymer produced through a relatively complex chemical route [18]. Another aspect worth mentioning is the necessity of using H_2 for the PMMA-based CVD process which can be considered as a drawback due to the high flammability of H_2 in the presence of oxygen. Furthermore, graphene formation on Ni foil is a well-known industrial heterogeneous catalysis process [19] and camphor, being a renewable feedstock, is an abundant and inexpensive carbon source [7]. Hence, production of graphene by CVD on a Ni foil using camphor is a viable alternative for fabrication at an industrial scale.

In this work, an efficient, low temperature (850 °C) and cost effective CVD process is employed, utilizing camphor as a solid precursor. The desired thickness of graphene films is achieved by turning off the heat and letting the system to cool down to room temperature on its own (estimated cooling rate up to 550 °C: 8 °C/min). This should be contrasted with the rather laborious flash cooling rates reported in the literature [13]. The produced graphene is characterized by means of a variety of analytical techniques such as scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and Raman. In-situ high temperature (HT) X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) measurements revealed the Ni surface morphology during annealing. The crystal quality and thickness of the formed graphene layers is investigated by Raman and X-ray photoelectron spectroscopies. The optimization of relevant parameters for graphene production such as camphor quantity and the deposition time could provide us a fine control of the thickness and structure of graphene.

2. Experimental details

2.1. Production of graphene layers

The CVD reactor was a quartz tube (length: 1 m, inner diameter: 4 cm) in which a polycrystalline Ni foil (99% purity by Aldrich), was placed. The tube was placed into a three-zone furnace which could be heated up to 1100 °C. The Ni substrate (1 cm × 1 cm) was polished by chemical–mechanical polishing before its introduction into the reactor. The CVD process consisted of two steps. Initially, a small quantity of camphor ($C_{10}H_{16}O$) in powder form was annealed at 200 °C and evaporated in the reactor. Then, using Ar as an inert carrier gas, the camphor molecules from the vapor phase flowed in the CVD reactor and were pyrolysed at 850 °C. The Ar gas flow rate was kept at a constant value of 800 ml/min. After 5 min of camphor decomposition the substrate was cooled down to room temperature at a rate of 8 °C/min (up to 550 °C) under an Ar atmosphere. Both steps are illustrated in Fig. 1 in which a sketch of the proposed CVD process is presented.

2.2. Characterization

2.2.1. X-ray photoelectron spectroscopy

XPS was used to examine the surface chemistry of the decomposed camphor molecules onto the polished polycrystalline Ni surface. The XPS measurements were carried out in an ultra high vacuum system equipped with a SPECS LHS-10 hemispherical electron analyzer using unmonochromatized MgKα (1253.6 eV) line. For a constant analyzer pass energy of $E_p = 36$ eV the full width at half maximum (FWHM) of the C1s XPS peak was 1 eV. The C1s peak was deconvoluted by Gaussian–Lorentzian components following a Shirley background subtraction.

2.2.2. Raman spectroscopy

MicroRaman (InVia Reflex, Rensihaw, UK) spectra were recorded with the 514.5 nm (2.41 eV) excitation, while the laser power was kept below 1 mW to avoid laser induced local heating on the studied samples. A ×100 objective with numerical aperture of 0.9 was used. All peaks in the Raman spectra of graphene were fitted with Lorentzians. The 2D linewidths together with 2D/G relative intensities were used to identify graphene monolayers.

2.2.3. X-ray diffraction

XRD measurements from the nickel substrate were carried out in a Bruker D8 ADVANCE diffractometer operating in θ–θ Bragg–Brentanno geometry. A high temperature furnace (XRK900, Anton Paar GmbH) was attached on the diffractometer in order to record diffractograms at elevated temperatures. The temperature was controlled through a temperature control unit (TCU750 Anton Paar GmbH) and was increased to 850 °C with a step of 5 °C/min and maintained there for 5 min in order to ensure temperature homogeneity over the sample. Then the system was cooled down to room temperature. During the thermal cycle the sample was under inert Ar atmosphere. Diffractograms were collected in the temperature range 25–850 °C, while at each temperature the beam was aligned in order to minimize instrument effects in the peak shapes and intensities. A CuK_a radiation source was used, operating at 40 kV and 40 mA, while the diffracted beam was collected with 1-D SSD LynxEye detector. Diffraction patterns were recorded in a continuous mode between 20° and 95° in the 2θ range with a step size 0.02° and scan time of 0.5 s/step.

2.2.4. Scanning electron microscopy

The morphology of the grown graphene samples on the Ni substrate was studied with variable pressure scanning electron microscope having a field emission gun (Zeiss SUPRA 35VP) operating at 15 kV. Grain size and orientation before and after the heat treatment of the substrate was measured with an EBSD system (HKL Nodlys II) attached on the SEM microscope. The accelerating voltage of the primary beam for the backscattered images was at 30 kV at a working distance of 15 mm and an aperture of 120 μm. EBSD 600 μm × 600 μm maps (300 × 300 points; step = 2 μm) were collected from different areas of the sample and analyzed by the TANGO software.

2.2.5. Atomic force microscopy

AFM was employed to assess the surface topography of the specimens. The instrument was operated at a tapping mode which employs a constant force method (i.e. the force between the sample surface and the AFM tip was kept constant by a feedback system while the surface beneath the tip was scanned). All specimens were imaged with the aid of multimode scanning probe microscopy (Veeco), using a nanoscope IIIa controller and a 120 μm × 120 μm magnet-free scanner (model AS-130VMF) developed by digital instruments with vertical range 5 μm and z-axis resolution 0.05 nm. The scan rate was 1 Hz. The cantilever's spring constant was 40 N/m. The shape of the silicon nitride tips was square pyramidal with radius of curvature ~10 nm and half angle ~15°. The images were processed with a linear plane fit in order to remove any sample tilt on them.