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# Substrate independent approach for synthesis of graphene platelet networks

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### Abstract

Graphene platelet networks (GPNs) comprised of randomly oriented graphene flakes two to three atomic layers thick are synthesized using a novel plasma-based approach. The approach uses a substrate capable of withstanding synthesis temperatures around 800 °C, but is fully independent of the substrate material. The synthesis occurs directly on the substrate surface without the necessity of any additional steps. GPNs were synthesized on various substrate materials including silicon (Si), thermally oxidized Si (SiO<sub>2</sub>), molybdenum (Mo), nickel (Ni) and copper (Cu), nickel–chromium (NiCr) alloy and alumina ceramics (Al<sub>2</sub>O<sub>3</sub>). The mismatch between the atomic structures of sp<sup>2</sup> honeycomb carbon networks and the substrate material is fully eliminated shortly after the synthesis initiation, namely when about 100 nm thick deposits are formed on the substrate. GPN structures synthesized on a substrate at a temperature of about 800 °C are significantly more porous in comparison to the much denser packed amorphous carbon deposits synthesized at lower temperatures. The method proposed here can potentially revolutionize the area of electrochemical energy storage by offering a single-step direct approach for the manufacture of graphene-based electrodes for non-Faradaic supercapacitors. Mass production can be achieved using this method if a roll-to-roll system is utilized.

Keywords: graphene platelet networks, plasma, synthesize

(Some figures may appear in colour only in the online journal)

# 1. Introduction

Graphene, a single layer carbon atomic sheet, is a novel twodimensional (2D) material attracting a lot of attention within the research community due to its unique physical properties [1]. With a combination of superior elasticity, mechanical stiffness, and high electrical and thermal conductivity [2, 3], graphene is being studied for a wide range of applications. Some potential applications include flexible electronics [4], high-frequency transistors [5], photodetectors [6], energy storage [7, 8], tissue enhancement additives [9], and biochemical applications [10, 11]. Currently, several approaches have been used to synthesize graphene, including mechanical and chemical exfoliation [12–14], chemical vapor deposition (CVD) [15], plasma enhanced chemical vapor deposition (PECVD) [16], epitaxial growth [17, 18], synthesis in microwave plasma [19, 20], laser ablation, and arc plasma-based synthesis [21–24].

Generally, these methods imply two types of synthesis mechanisms, namely substrate-free synthesis of graphene and on-surface synthesis of graphene [25]. On-surface methods of graphene synthesis, such as CVD, PECVD and epitaxial graphene growth, are associated with the production of large-area planar pristine graphene structures. This type of graphene is used for fabrication of ultra-high-speed, low-power graphene-channel field effect transistors and transparent

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electrodes [3, 26-36]. Currently there are two widely recognized and well-studied mechanisms of CVD synthesis of graphene. The first mechanism is dominant when materials characterized by a high solubility of carbon are utilized as a growth substrate, e.g. Ni [37]. In this case the carbon atoms dissolve in the substrate material first and then they precipitate on the substrate surface during the substrate's cooling. These precipitated atoms form a graphene film on the substrate surface. Grown graphene films are usually limited to the grain size of the substrate and contain many layers. The second mechanism of graphene growth is employed when materials characterized by a low solubility of carbon are utilized for the growth substrate, e.g. Cu [26]. In this case graphene is surface-catalyzed as proposed by Ruoff et al [14]. It was shown that synthesis on Cu substrates is basically self-limiting on the production of a single layer graphene film of extraordinary quality. Regardless of the exact synthesis mechanism, a close structural match of the substrate and graphene is required for synthesizing a high quality graphene film [38, 39].

Methods of synthesis of multi-layered graphene structures in chemical exfoliation, in microwave and arc plasma processes have been demonstrated previously [13, 14, 19– 21, 24]. Properties of the multi-layered graphene were analyzed and compared with that of the single-layered graphene using nanocharacterization techniques including Raman spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy [13, 14, 19–21, 24, 26, 40–43].

Therefore, the surface methods of graphene synthesis require the presence of a structural match between the substrate and the graphene film growing on it. In this article, we report a new approach of graphene synthesis on substrate surface, which is fully independent from the substrate material regardless of the degree of the original mismatch in the atomic structures of graphene and the underlying surface. This method only requires the substrate to be able to withstand the synthesis temperature of about 800  $^{\circ}$ C.

# 2. Methods

Synthesis was conducted in a cylindrical stainless steel vacuum chamber, which was 270 mm in length and 145 mm in diameter. The chamber was pumped with a mechanical pump, Alcatel-2033, to  $10^{-2}$  Torr. The chamber was equipped with a pair of carbon discharge electrodes made of Poco EDM-3 graphite. The anode and cathode had a diameter of 3 mm and 12 mm, respectively. Electrodes were separated about 4–5 mm from each other. The arc was ignited and supported by a Miller Goldstar 500 s welder power supply. The arc current, measured using a current clamp probe, and arc voltage signals were filtered and recorded on a digital oscilloscope. Arc durations were <10 s and arc currents of about 70 A were utilized.

Substrates were installed inside the chamber about 5 cm away from the electrodes' gap radially (see figure 1). The substrates were ohmically heated and the temperature was monitored using type K thermocouples attached to the backside of the substrate (not exposed to the discharge electrodes).

The substrates were evaluated using the following nanocharacterization tools: SEM (Carl Zeiss Sigma VP Field Emission and FEI LV FEG SEM 'Teneo'), Raman spectroscopy (Horiba LabRAM HR), AFM (Asylum MFP-3D) and x-ray photoelectron spectroscopy (XPS).

#### 3. Results and discussion

The Raman spectra (recorded with 532 nm excitation laser) of the synthesized structures are dependent on the substrate temperature (T), and are presented in figure 2(a). The observed spectra at  $T = 850 \,^{\circ}$ C are quite typical for graphene containing structures. One can see from figure 2(a) that it consists of three prominent bands, namely D, G and G'-band at  $1350 \text{ cm}^{-1}$ ,  $1580 \text{ cm}^{-1}$ ,  $2700 \text{ cm}^{-1}$  respectively, and smaller intensity bands D',  $G^*$ , G + D, 2D' at  $1620 \text{ cm}^{-1}$ ,  $2450 \text{ cm}^{-1}$ ,  $2930 \text{ cm}^{-1}$  and  $3230 \text{ cm}^{-1}$  respectively. The G, G' and G\*-bands are associated with phonon modes in sp<sup>2</sup> hexagonal carbon networks, while the spectra bands D', G + D, 2D' are associated with the presence of defects (we are following bands' notation given in [40]). The defects are caused by various factors, namely the proximity to graphene sheet edges, orientation of the sheet with respect to the laser beam and the presence of dopant atoms [40-43].

Now, let us discuss the evolution of band intensities with an increase of the substrate temperature (*T*) shown in figure 2(a). The most prominent feature is the increase of the intensity of G'-band at 2700 cm<sup>-1</sup> with the rise in *T*. Indeed, the ratio of G'-band intensity to that of the G-band I(G')/I(G)was about 0.1 at T = 500 °C, while the ratio increased to about 0.9–1 at 850 °C. In addition, one can see that the D and G-bands were broad and partially overlapped at the lower temperature *T* at about 500 °C, while an increase of temperature led to sharper and well-separated peaks at T = 850 °C. Such evolution of spectra is typical for the transition from amorphous sp<sup>3</sup> carbon structures (a-C) to sp<sup>2</sup> bonded hexagonal carbons as indicated in many previous research works [44–46].

The number of layers in graphene containing structures was analyzed using Raman spectra following the methodology described in [40-43]. The G'-band of a monolayer graphene is a single Lorentzian peak. A G'-band with a convolution of multiple peaks represents multi-layered graphene, and this relationship will lead to a larger overall peak width and smaller amplitude. Full width at half maximum (FWHM) is minimal for monolayer graphene (about  $24 \text{ cm}^{-1}$ ) and FWHM is larger for multi-layered graphene. The FWHM of the overall G'-band is  $\sim$ 45–60 cm<sup>-1</sup> for turbostratic multilayer graphene (which is rotationally random stacked individual graphene layers) and the FWHM of G'-band is  $\geq 100 \text{ cm}^{-1}$  for double, triple and four layered graphene in Bernal stacking. Our experiments conducted at  $T = 850 \,^{\circ}\text{C}$ yielded the FWHM of the G'-band of about  $100 \text{ cm}^{-1}$ , which is consistent with multilayer layer films. The number of layers in the multi-layered graphene was also characterized by the



Figure 1. (a) Schematic of the experimental set-up and (b) the heater assembly.

relative intensity of the G'-band with respect to the G-band, namely I(G')/I(G). For pure monolayer graphene the ratio I(G')/I(G) is typically large (about 3–5). The increase of the layer number in the multi-layered graphene causes the reduction of the I(G')/I(G) ratio. Indeed, I(G')/I(G) ratio for double layered graphene is about 1, and 0.5–1 for triple layered graphene. Further increase of the number of layers causes an additional decrease of the I(G')/I(G) ratio, and the ratios less than 0.1 are typical for highly oriented pyrolytic graphite. The experiments conducted for T = 850 °C yielded the FWHM of the G'-band of about 100 cm<sup>-1</sup> and I(G')/I(G) = 1, which is consistent with two- to three-layer graphene sheets.

Typical SEM images of the nanostructures synthesized at the corresponding substrate temperatures are also shown on the lower row of figures 2(b) and (c). The SEM images were obtained with an upper in-lens detector (T2) with 5 kV and 25 pA. One can see that the morphology of the synthesized films had changed dramatically from dense amorphous structures at lower temperatures T = 500 °C, to very porous structures comprised of a large number of randomly oriented tangled flakes at T = 850 °C. Figures 2(e) and (f) show the TEM and HRTEM images (obtained using an FEI 'Talos' F200X operated at 200 kV) for the GPNs, and typical graphene structures could be observed in these images.

XPS results obtained for the nanostructures synthesized at temperatures of 500 °C and 850 °C are presented in figure 2(d). The main component in the C 1s spectrum of the sample prepared at higher synthesis temperatures (850 °C) has FWHM of 0.67 eV; a broad shake-up satellite is detected at approximately 290 eV; the area of the shake-up peak was found to be in the range of 10% of the main carbon peak. For the sample prepared at the lower temperature (500 °C), the FWHM is larger (0.96 eV) and no shake-up satellite can be detected. These results indicate the formation of graphenelike structures at 850 °C in contrast with a-C structures at 500 °C. The inserted table in figure 2(d) shows the elemental composition of the nanostructures. One can see that the structures synthesized at the higher temperature were of higher purity with fewer admixtures. Therefore, based on the above analysis we may conclude that nanostructures synthesized at T = 850 °C are comprised of a large number of randomly oriented and tangled graphene flakes having on average a thickness of about two to three atomic layers. These structures are referred to as GPNs in the following description. The synthesis conducted at lower temperatures led to the production of primarily a-C structures.

Let us now trace the evolution of the synthesized structures with change of substrate temperature. In this experiment we electrically heated one side of the rectangular Si sample as it is schematically shown in figure 3(a). This resulted in a temperature gradient along the sample. The temperatures were measured using three thermocouple probes brought in contact with the back of the Si sample as shown in figure 3(a). Distribution of the I(G')/I(G) ratio and the sample thickness are shown in figures 3(c) and (d) respectively. One can see that the transition from an a-C to GPN structure is occurring in the temperature range T of about 700  $^{\circ}$ C–800  $^{\circ}$ C according to the analysis of the I(G')/I(G) ratio of the Raman spectrum shown in figure 3(c). In addition, the transition from a-C to GPN was accompanied by the simultaneous increase of the deposit's thickness as shown in figure 3(d). This increase of the deposit's thickness cannot be related to the non-uniformity of the incoming flux from the arc. Indeed, the thickness distribution along the unheated (room temperature) substrate was measured to be uniform along the sample within 5% divergence (the deposit consisted of purely a-C structures in this case), which shows the uniformity of the incoming carbon flux. Therefore, it can be hypothesized that GPN structures grown on the heated side of the substrate are characterized by a significantly smaller density compared to the a-C structures grown on the colder side. This conclusion is in full agreement with the SEM observations (see figure 3(e)) showing that the GPN structures on the heated side of the substrate were significantly more porous in comparison with the much denser packed a-C deposits on the colder side.

It is important to note that the synthesis approach presented here is purely independent of the substrate material. Indeed, different materials were utilized in the synthesis including pure Si and thermally oxidized Si wafers (SiO<sub>2</sub>), molybdenum (Mo), nickel (Ni) and copper (Cu), nickel-



**Figure 2.** (a) Raman spectra of graphene sheets synthesized directly on Si substrate at T = 500 °C-850 °C. (b) and (c) Typical SEM images of the structures synthesized at 500 °C and 850 °C respectively. (d) XPS spectra of the structures at 500 °C and 850 °C. (e) TEM images and (f) HRTEM images of the GPNs synthesized at 850 °C.



**Figure 3.** Evolution of the deposit grown at different substrate temperatures using uniform incoming carbon flux. (a) Schematics of the silicon substrate equipped with three thermocouple probes. (b) Temperature distribution along the sample, (c) I(G')/I(G) ratio indicating presence of GPNs in the hotter zone T > 700 °C–800 °C and an a-C deposit in a colder zone. (d) Thickness of the deposit indicating more a porous structure GPN rather than an a-C deposit. (e) SEM images of porous GPN synthesized in the hot zone and an a-C deposit in the colder zone.

chromium (NiCr) alloy and alumina ceramics (Al<sub>2</sub>O<sub>3</sub>). Raman spectra similar to that of GPN structures presented in figure 3(c) were observed for all tested substrate materials. Ratios of I(G')/I(G) = 0.8-0.9 for different substrate

materials synthesized at T = 800 °C were observed as shown in figure 4, which indicates that GNP structures were synthesized on all tested substrate materials.



**Figure 4.** I(G')/I(G) ratio for graphene films synthesized on different substrates.

Another interesting observation is related to the influence of the carbon deposit thickness on the synthesized structure properties prepared at T = 850 °C. Figure 5(b) shows the thickness distribution of the deposit along the Si wafer substrate which was heated to T = 850 °C. Variation of the thickness was achieved by shielding the part of the substrate from the incoming plasma flux as shown schematically in figure 5(a). The corresponding Raman spectra taken at different locations along the substrate are shown in figure 5(c). One can see that the thickness of the deposit in the unshielded region was quite large, namely about  $0.7-1 \,\mu\text{m}$ , indicating that the contact with the substrate was eliminated and newly grown carbon structures were actually synthesized on top of previously deposited ones rather on the substrate material directly. These thick deposits yield high ratios I(G')/I(G) $\sim$  1, which identifies them as GPN structures similar to that shown in figure 1 for T = 850 °C. In contrast, one can see that the shielded parts of the substrate (h about 10 nm) are characterized by the low ratios  $I(G')/I(G) \sim 0.4$  identifying them as a-C structures. According to the XPS analysis, no shake-up peak was detected in the shielded region in contrast to the unshielded region where a prominent shake-up peak was observed (with an area approximately 10% of the total carbon peak area). These observations can be interpreted using the fact that the structures growing directly on the substrate are characterized by the mismatch of the lattice parameters of the substrate and graphene, thus producing a-C deposit, while further growth is occurring directly on top of a pre-deposited carbon buffer layer. The mismatch was gradually eliminated in the buffer layer while its thickness grew from 0 to about 100 nm, and finally led to synthesis of GPN structures regardless of the substrate's material.

Therefore, we conclude that GPNs can be synthesized on any substrate material capable of withstanding the synthesis temperature of about 800 °C. The carbon buffer layer is grown on top of the substrate material, which gradually eliminates the structural mismatch between the sp<sup>2</sup> honeycomb carbon networks and the substrate material. The mismatch vanishes once the carbon buffer layer thickness reaches



**Figure 5.** Evolution of the synthesized carbon deposit structure versus thickness conducted using shielded sample. (a) Geometry sketch for the shielded sample (b) Thickness distribution showing *h* decrease in the shielded area. (c) Raman spectra evolution in shielded versus unshielded areas. (d) I(G')/I(G) ratio versus thickness *h* indicating amorphization for thin films possibly due to mismatch between graphene and sample material structure.

about 100 nm, and then the synthesis of GPN structures begin.

The approach presented here can revolutionize the area of graphene-based electrodes' manufacturing for electrochemical energy storage. Indeed, conventional preparation of graphene-based electrodes for supercapacitors involves multistep process including synthesis, reduction of graphene oxide in liquid solution, binding the graphene structure to the electrode surface etc. In contrast, the approach presented here is a single-step direct process characterized by good adhesion to the substrate and it allows for mass production if a roll-toroll system is used.

In conclusion, this paper presents a new approach of substrate-based graphene synthesis. The approach is truly substrate independent and can be conducted with any substrate material capable of withstanding a synthesis temperature of about 800 °C. The structural mismatch between the graphene and the substrate material is eliminated when the thickness of the intermediate carbon buffer layer has increased to about 100 nm. The synthesized GPNs yield high ratios  $I(G')/I(G) \sim 1$  on a Raman spectrum. GPN structures are a significantly more porous compared to a-C structures synthesized at lower temperatures (500 °C).

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