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Nano-graphene structures deposited by N-IR pulsed laser ablation of graphite on Si

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Abstract

Thin nano-structured carbon films have been deposited in *vacuum* by pulsed laser ablation, from a rotating polycrystalline graphite target, on Si ⟨1 0 0⟩ substrates, kept at temperatures ranging from RT to 800 °C. The laser ablation was performed by a Nd:YAG laser, operating in the near IR (λ = 1064 nm).

X-ray diffraction analysis, performed at grazing incidence angle, both in-plane (ip-gid) and out-of-plane (op-gid), has shown the growth of oriented nano-sized graphene particles, characterised by high inter-planar stacking distance ($d_{\xi} \sim 0.39$ nm), compared to graphite. The film structure and texturing are strongly related both to laser wavelength and substrate temperature: the low energy associated to the IR laser radiation (1.17 eV) generates activated carbon species of large dimensions that, also at low T (∼400 °C), easy evolve toward more stable sp^2 aromatic bonds, in the plume direction. Increasing temperature the nano-structure formation increases, causing a further aggregation of aromatic planes, voids formation, and a related density (by X-ray reflectivity) drop to very low values. SEM and STM show for these samples a strongly increased macroscopic roughness. The whole process, mainly at higher temperatures, is characterised by a fast kinetic mode, far from equilibrium and without any structural or spatial rearrangement.

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1. Introduction

Carbon-based new materials in the planar aromatic configuration, like carbon nano-tubes, graphite intercalation compounds, fullerenes, and ultrathin graphite films, are gaining more and more scientific interest since they exhibit many unexplored new properties such as high electron mobility and anomalous quantum Hall effect [1–4]. These outstanding characteristics are related to the structure of a two-dimensional form of carbon, named ‘‘graphene’’: a single hexagonal carbon layer, isolated for the first time by Novoselov et al. [1], that is the building block for all these materials. The unusual electronic properties (mobilities of ∼20 000 cm^2/V s, an order of magnitude higher than that of modern Si transistors) of this new material seems to open the possibility towards a ballistic transport on submicron distances ‘‘the holy grail for any electronic engineer’’ [5,6]. Other nano-carbon materials like stacking nano-graphene layers in an amorphous matrix or quantum confined sp^3/sp^2 nano-layers seems also very promising for field emission displays and other electronic applications [7–9]. Many authors reported increased electronic properties as an effect of thermal annealing of amorphous carbon films [10–14]. This effect was generally related to an increase in π bonds and specifically to aromatic nano-clustering and orientation [10,11,15,16]. Electronic transport and field emission are promoted along the graphite basal plane owing to the asymmetric distribution of the electronic charge associated to the π band [11,14,15,17]. A cluster–cluster interaction was claimed to be the main origin of increased conductivity, by means of a hopping or ‘‘percolative’’ process between conductive sp^2 sites inside an amorphous matrix [10,11].

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Our aim is to explore the optimal experimental condition of pulsed laser deposition (PLD) to obtain carbon film with a high percentage of sp^2 coordination and controlled nano-structure. PLD is one of the most useful techniques in thin film technology owing to many properties and advantages [18–20], the most relevant in our case being the ability to produce unique or metastable materials that cannot be made under normal thermal conditions.

Many research efforts have been devoted to understand the ablation process and formation of clusters in the plasma plume [21], since the laser produced plasma plays an essential role in determining the ultimate characteristics of the deposited films [20].

In this paper we investigated the influence of a low energy IR laser wavelength, at increasing fluence, associated also to a temperature variation, on the structure, morphology and density of the deposited films. The study was performed by grazing incidence X-ray diffraction (GI-XRD) operated both out-of-plane (op) and in-plane (ip) configuration, X-ray reflectivity (XRR), SEM and STM.

2. Experimental

2.1. PLD

Carbon thin films, with thicknesses ranging from ~0.4 to ~1.0 μm, were grown by PLD. The carbon plume was produced irradiating a high purity polycrystalline graphite target with a Nd:YAG laser (Quanta Ray), at a wavelength $\lambda = 1064$ nm, a pulse duration $\tau = 7$ ns, and repetition rate $\nu = 10$ Hz.

The laser beam was focused, at an angle of 45°, on a continuously rotating target, in order to guarantee a homogeneous consumption, during the ablation process. Deposition runs were performed at different laser energies, namely at 250, 350 and 450 mJ/pulse (higher energy ~650 mJ was completely disruptive) with a laser spot on target of ~3.2 mm^2, leading to laser fluences of ~7.8, 11 and 14 J/cm^2, respectively. The laser spot size is independently controlled by a fine positioning of the last focusing lens on the optical bench with respect to the vacuum chamber. The graphite target was accurately polished to prevent the occurrence of large particles (debris) within the plume. Droplet incorporation has been also prevented by a shutter system at the early stage of deposition. Single crystal, n-doped silicon ⟨1 0 0⟩ wafer (10–16 mΩ cm) was used as substrate. The substrates were mounted on a holder, parallel to the target at a distance of 5 cm. The chamber was evacuated to a residual pressure of 10^{-4} Pa and the substrate heated by lamps to the deposition temperature ranging from RT to 800 °C.

2.2. X-ray techniques

GI-XRD and specular X-ray reflectivity (S-XRR) measurements were carried out with a lab facility at CNR-IMM (Bologna) with a SEIFERT MZ VI diffractometer and Cu Kα radiation.

For the GI-XRD laboratory scans, two settings configurations have been used so as to obtain reflections coming:

- From the aromatic graphite rings (1 0 0, 0 1 0) [out-of-plane grazing incidence diffraction: op-gid].
- From the stacking graphene parallel layers (0 0 2) [in-plane grazing incidence diffraction: ip-gid].

A detailed description of the corresponding configurations are reported elsewhere [22].

For S-XRR, the Soller slits used for GI-XRD, were replaced by a very narrow slit of 0.01° aperture and sample and detector were scanned over the angular range of interest in the ratio 1:2.

Information on the crystalline phases, crystallite orientation and size were obtained from GI-XRD, the last data being based on the evaluation of the peak broadening; the film mass density was extracted from S-XRR data using a home developed software based on the Parratt's formalism.

2.3. SEM and STM characterisation

The film morphology and thickness (cross-section) have been studied by a Philips XL30 SEM apparatus. STM images were recorded with an OMICRON equipment, operating in ultrahigh vacuum and at room temperature.

3. Results

The micrographs of op-gid and ip-gid spectra for samples deposited at 250 mJ/pulse (α), at increasing substrate temperature, are shown in Fig. 1a and b.

At RT the film is amorphous. At $T \geq 400$ °C, the films begin crystallising, as shown by the appearance of 0 0 2 and 1 0 0 graphite peaks, at ~23° and ~43° (ip-gid spectra) and at ~43° in op-gid spectra.

The broad intensity bumps at ~20° (op-gid) come from a partial atomic arrangement of the C atoms in the amorphous phase (onset of visible short range order).

The lack of the 0 0 2 graphite peaks in the op-gid measurements suggests that the C nano-particles are strongly oriented, with their č-axis parallel to the sample surface (Fig. 1c). Very similar spectra (not reported for the sake of brevity) have been obtained for samples deposited at increased laser fluence of 350 mJ/pulse (δ) and 450 mJ/pulse (β).

The fraction of amorphous phase can be distinguished from the crystalline fraction, in the sample deposited at $T = 800$ °C (Fig. 1c). The intensity over the back-ground of the bump at ~20° (op-gid spectrum) is about 10 times lower than the net 0 0 2 peak intensity (ip-gid spectrum), while the intensities of the 1 0 0 peaks are almost the same in both spectra. This small contribution can be tentatively associated to the amorphous phase. The δ and β series show the same phenomenon. That means the films are not fully crystallised even at higher T.

The preferred orientation of the C nano-particles is confirmed for all the samples by the detection in the ip-gid